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(54) Title: IN SITU PHOSPHATIZING AND SILICATING COATINGS AND METHOD OF MAKING SAME

(57) Abstract: A single coat that is an in situ self-phosphatizing paint, the coat having a phosphatizing reagent, a silicating agent, and a metal chelating agent and a substrate having the coating on a surface thereof. An additive package for creating an *in situ* self-phosphatizing paint, the package having a phosphatizing reagent and a metal chelating agent and/or a silicating agent is provided. Also provided is a method of forming an *in situ* self-phosphating / silicating paint can promote a selective polymerization reaction, form a dense paint film, widen the useful thermal curing temperature ranges, and prevent "paint yellowing" of certain paint systems.

**IN SITU PHOSPHATIZING AND SILICATING COATINGS,
AND METHOD OF MAKING SAME**

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BACKGROUND OF THE INVENTION

1. Technical Field

The present invention relates to an *in situ* phosphatizing and simultaneously silicating coating. More specifically, the present invention provides a coating that protects a metal surface by forming a non-conductive phosphate and silicate layer in-situ on the surface that inhibits corrosion.

2. Description of Related Art

Surface treatments for substrates, such as metals, are commonly utilized to inhibit corrosion and improve adhesion of subsequent coatings. One such surface treatment is a phosphate conversion coating that phosphatizes the surface by producing a non-conductive phosphate crystalline/amorphous layer on the surface that insulates the metal from subsequently applied coatings and provides a topography having chemical functionality for reacting with the coating.

Representative of the phosphate conversion coating processes are an iron phosphate coating process and a zinc phosphate coating process that use a bath of iron phosphate and zinc phosphate, respectively. Both processes require multiple steps including meticulous cleaning, pretreatment of the surface, dipping in the bath, and rinsing. The steps are then followed by application of the coating. If the cleaning pretreatment is not properly performed, the surface can be defective in that it can have less corrosion protection, and hence can be more likely to corrode than a non-defective surface. The iron phosphate coating process requires close chemical control of the bath to achieve reproducibility and satisfactory results. The zinc phosphate coating composition is more complex and expensive than the iron phosphate coating process and requires additional chemical additives. Some of

these additives are environmentally hazardous. The removal and disposal of sludge produced in the bath is a serious environmental problem. Further, if the sludge contaminates the surface to be coated, then the coated metal surface can be defective.

5 In the multi-step processes, phosphate coatings are quite porous and begin to degenerate shortly after application if not quickly recoated with a suitable primer. For example, in less than four days, the unprotected iron phosphate film can deteriorate to a point where there is little corrosion protection.

10 The multi-step processes can also include a chromic acid rinse to seal the phosphatized metal surface prior to applying the coating. The primer coating contains a large amount of chromates that serve as anti-corrosive pigments. The chromic acid and chromates are hexavalent chromium compounds that are highly toxic, carcinogenic, and therefore undesirable.

15 The multi-step processes also utilize a large amount of volatile organic compounds (VOCs) that are hazardous to the environment.

20 In an attempt to provide better coating, individuals have created coating compositions containing phosphoric acid and rust-inhibiting derivatives thereof as rust-resisting agents for use in paint. The compositions lack an additive package having a stable and compatible phosphate forming agent, a selective cross-linking catalyst, an ion-exchanged silicate forming agent, and a metal chelating agent in the paint, all of which form a more stable and therefore useful coating composition.

25 Additional attempts include a thermosetting organic coated sheet metal product having a partially cured coating which bonds to a metallic substrate. The coating requires that the part being coated must subsequently be treated with a protective and/or decorative coating applied thereon as the top or finish coat. There is no disclosure of a coating that can prevent corrosion absent further treatments.

 Synthetic resins and coating compositions for coating metal substrates, particularly food and beverage cans have also been developed. The resin includes the reaction product of a water insoluble phenolic resin or a water insoluble amino

resin with an epoxy resin and a phosphoric acid. The reaction of the phenolic or amino resin with the epoxy and acid occurs prior to the application of the composition on a substrate.

The Lin et al. reference (Chemistry of a Single-Step Phosphate/Paint System, Ind. Eng. Chem. Res., Vol. 31, No. 1, 1992) discloses a single-step phosphate/paint system that utilizes phosphoric acid, a resin, and a cross-linking agent. The phosphoric acid causes the paint system to be unstable and only partially compatible with the paint film forming resins because the acid reacts with the other paint components or non-specifically catalyze the reaction of the components. The stability and compatibility of the paint disclosed in the Lin et al. patent are limited because only clear, unpigmented paints have been produced. Further, the paint disclosed in the Lin et al. patent requires a large amount of solvent, which increases the VOCs that are miscible with both the phosphoric acid and the other components. If when following the methods of the Lin et al. patent a paint is formed that utilizes a resin and cross-linking agent combination other than polyester, e.g. melamine enamel or a pigment, then the paint becomes useless in a short period of time because of the reactions that occur within the paint composition, e.g., the self-condensation of the cross-linking agent, the co-condensation reaction of the resin with the cross-linking agent, and aggregation of the pigment due to the highly acidic (pH<2.0) condition of the components prior to application to the surface.

It would therefore be useful to develop a single coat, *in situ* self-phosphatizing paint that is easy to use, does not require meticulous cleaning of the surface, eliminates the need for separate phosphate conversion and subsequent chromate treatment and coating steps, eliminates the bath, reduces VOCs, is stable, and can be pigmented. Preferably, the paint can be used to protect plastic and wood surfaces in addition to metal surfaces.

SUMMARY OF THE INVENTION

According to the present invention, there is provided a single coat *in situ* self-phosphatizing / silicating paint, the paint including a phosphatizing reagent and at least one of a silicating agent and a metal chelating agent and a substrate having the

coating on a surface thereof. An additive package for creating an *in situ* self-phosphatizing paint, the package having a phosphatizing reagent and a metal chelating agent and/or silicating agent is provided. Also provided is a method of forming an *in situ* self-phosphatizing single-layer coating by combining a phosphatizing reagent and a metal chelating agent and/or silicating agent with a coating. The *in-situ* phosphatizing reagents (ISPRs) provided herein can generate metal phosphate layer *in-situ* and act as an acid catalyst in polyester-melamine coatings.

BRIEF DESCRIPTION OF THE DRAWINGS

Other advantages of the present invention are readily appreciated as the same becomes better understood by reference to the following detailed description when considered in connection with the accompanying drawings wherein:

Figure 1 is a schematic showing the possible channels of pollution arising from the coating in the prior art;

Figures 2 A-C are graphs showing the refractive FTIR spectra of the ISPR-generated phosphate layers generated *in situ* on cold rolled steel (Figure 2A), 2024-T3 aluminum alloy (Figure 2B), and Ti-6Al-4V titanium alloy (Figure 2C);

Figures 3 A-D are photographs showing the results of saltwater immersion tests (six days soaking in 3% NaCl solution) for control panels (Figures 3A and C) and ISPC (Figures 3B and D) paint formulations on bare (Figures 3A and C) and chromated (Figures 3B and D) titanium alloy coupons;

Figure 4 is a graph showing the bode-magnitude plot of painted panels after soaking in 3% salt solution for 72 hours; curves a and b represent the ISPC formulation on chromated and bare aluminum, respectively; curves c and d represent the control formulation on chromated and bare aluminum, respectively;

Figure 5 is a graph showing the bode-magnitude plots of the final impedance for painted panels after soaking in 3% salt solution for 2500 hours;

Figures 6 A-F are photographs showing the results of a 100-hour salt spray (fog) test; Figures A-C show coupons coated with an alkyd control formulation and Figures D-F show coupons coated with an ISPC alkyd formulation;

Figure 7 is a photograph showing the results of a 4500-hour salt fog test (ASTM B117) on a chromate free primer over 2024-T3 Clad Alodine 1200 treated aluminum alloy;

Figure 8 is a graph showing FTIR reflectance spectrum of the metal-phosphate layer generated by the ISPR on polished 3003 Aluminum;

Figures 9 A-E are micrographs (5X with 80X inserts) showing the morphology of ISPC-generated phosphate layers on bare polished aluminum;

Figures 10 A-D are photographs showing the results of adhesion tests for EIS sample panels soaked for 102 days in 3% NaCl solution; Figure 10A shows the control painted on bare aluminum; Figure 10B shows the control painted on chromated aluminum; Figure 10C shows the ISPC painted on bare aluminum; and Figure 10D shows the ISPC painted on chromated aluminum;

Figures 11A-F are photographs of 3004-hour salt spray testing panels of aluminum alloys;

Figures 12 A and B are photographs showing the results of a 1000 hour salt spray testing panels painted with AD9318/AD2298 chromate primer, Figure 12A shows the results when the panel is 2024-T3 bare/alodine 1200 and Figure 12B shows the results when the panel is 2024-T3 bare/AFP;

Figure 13 is a graph showing the bode-magnitude plot of painted panels after soaking in 3% NaCl solution for 1000 hours;

Figures 14 A-D are SEMS scans of iron phosphate layer on a CRS surface produced by ISPR-2 (Figure 14A) and ISPR-1 (Figure 14B) and Figures 14C and D show the corresponding EDX spectra of Figure 1A and B respectively;

Figure 15 is a graph showing Nyquist plots of 2024-T3 bare Al panels measured after soaking in a 3% NaCl solution for 1000 hours;

Figure 16 shows TGA scans of polyester-melamine paint films catalyzed by (Figure 16a) 3 % ISPR and (Figure 16b) 3 % Cycat 4040 (p-TSA); the ISPR-catalyst paint is thermally stable; more thermal decomposition occurs when using p-TSA as the catalyst; and

Figure 17 shows painted galvanized steel of polyester-melamine catalyzed by (Figure 17a) ISPR and (Figure 17b) p-TSA cured at 400 °C for 40 seconds, a "paint yellowing" is observed in (Figure 17b), but not in (Figure 17a).

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

Generally, the present invention provides a coating that includes therein a phosphatizing reagent, which also acts as a polymerization catalyst, a silicating agent for silicate layer formation via an ion-exchange mechanism, and/or a metal chelating agent that can inactivate the corrosion sites as an additive package for addition to a coating or paint. In other words, the coating of the present invention can be formulated as follows: 1. phosphatizing reagent, a metal chelating agent, and a silicating agent; 2. phosphatizing reagent and a metal chelating agent; or 3. phosphatizing reagent and a silicating agent. The additive package of the present invention is suitable for use in a single coat, self-phosphatizing and silicating coating that can react *in situ* on a surface of a substrate to provide a non-conductive phosphate and silicate layer to inhibit corrosion of the substrate, with the paint also forming a topcoat that reacts with the layer to improve adhesion to the topcoat. One benefit of the present invention is that polymerization occurs independently and simultaneously with the phosphatization and silicate formation. In the preferred embodiments, the *in situ* phosphatizing reagents (ISPRs) are designed with a dual purpose of catalyzing the crosslinking reaction of polymer film and also providing phosphate formation of the surface of the metal substrates.

The term "*in situ*", when referring to the paint, indicates that substantially no irreversible chemical reactions occur prior to the application of the paint to the substrate and that substantially all of the irreversible chemical reactions occur when the paint is on the substrate.

5 The term "irreversible chemical reaction", as used herein is intended to include, but is not limited to, a reaction that cannot be reversed under ambient conditions and times to yield constituents capable of subsequent reaction.

10 The term "ambient condition", as used herein is intended to mean a temperature in the range of about 50° to about 90° F and a pressure of about atmospheric pressure.

The term "corrosion", as used herein is intended to refer to the degradation of the substrate as, for example, the electrochemical degradation of metals or their alloys, the rotting of wood and the breakdown of the chemical bonds of plastics.

15 The term "coating", as used herein is intended to refer to a layer of material applied to an substrate's surface and the material itself. The coating can be a paint or other similar substance.

The term "single coat", as used herein is intended to refer to one layer. In other words, the coat is not applied in multiple layers, but is instead a solitary layer that is applied in a single step.

20 The term "substrate", as used herein is intended to refer to any article to which the coating of the present invention can be applied. This can include, but is not limited to, metals.

The term "self-phosphatizing" as used herein is intended to refer to compound that is capable of phosphatizing without the addition of further compounds.

25 The application of the paint to a surface of the substrate produces a coating that includes a non-conductive phosphate and silicate layer contiguous with the surface to thereby inhibit corrosion of the surface. The layer results from phosphate chemistry and silane chemistry. For phosphate chemistry, when the paint is applied

to the substrate and exposed to heat, ultraviolet light, or air-drying, the active phosphatizing reagent is generated. The reagent migrates to the surface and reacts with the substrate to provide the non-conductive phosphate layer that provides the corrosion protective barrier and which has good adhesion to the substrate. The reaction results in chemical functional groups that react with the resin and the cross-linking agent to form phosphorus, oxygen, and carbon (P--O--C) covalent bonds to improve adhesion of the topcoat to the layer and hence the substrate. The topcoat is the result of polymer chemistry. The reagent also catalyzes polymerization of the resin and cross-linking agent that leads to dense and lesser defective paint films. The ISPC coated films are thermally stable due to a preferred co-condensation polymerization reaction. The organofunctional silanes chelate the metal surface active sites and inactivate the metal corrosive sites. The organofunctional silanes act as polymer coupling agent and paint pigments dispersants.

The "organic phosphates (or organic phosphonates)" used in the coating of the present invention are more compatible and easier to be dispersed in paint systems than a pure phosphoric acid. The organic phosphates (or organic phosphonates) are acidic and can react prior to application to the substrate if the reagents are not properly dispersed in the paint. The reaction can be a self-condensation reaction of the cross-linking agent, a co-condensation reaction of the resin with the cross-linking agent, or particle aggregation of the pigment. The amine helps to stabilize the organic phosphate (or organic phosphonate) and inhibit these reactions occurring prior to application to the substrate. For an acid catalyzed polymerization reaction, the organic phosphates (or organic phosphonates) are the desired catalysts and can substitute or partially substitute p-TSA, what are currently used in the market.

Suitable phosphatizing reagents for use in the present invention include organic phosphoric acids, organic phosphonic acids, and esters thereof. More specifically, suitable phosphatizing reagents include mono- and di-alkyl phosphoric acid, mono-alkyl phosphonic acid, mono- and di-phenyl phosphoric acid, mono-phenyl phosphonic acid, mono- and di-aryl phosphoric acid, mono-aryl phosphonic acid, the like and mixtures and esters thereof. Preferably, the alkyl groups have 1 to

approximately 12 carbon atoms. Preferred reagents are mono- and di-phenyl phosphoric acid, mono- phenyl phosphonic acid, and esters thereof.

Representative metal chelating agents include mono, di, and tri - organofunctional silanes. Suitable organofunctional groups include, but are not limited to, epoxy, vinyl, amino, mercapto, methacryl, etc. Other metal chelating agents are also effective, such agents can include, but are not limited to, diethyldithiocarbamic acid, and salts thereof.

Suitable ion-exchanged silica gels for use in the present invention include all particle sizes and are commercially available and known to those of skill in the art.

To further increase the stability of the reagent, the coating composition can include additional components. Examples of such components include, but are not limited to, resins, an amine, pigments, surfactants, extenders and fillers, accelerators, and solvents. The resins and cross-linking agents with which the additive package is admixed can be the same as those utilized in the coating composition. Other components of the additive package or the coating can include, but are not limited to, a solvent (preferably a hazardous air pollutant -(HAP-) free solvent), a surfactant, and metal salts.

Suitable surfactants for use in the present invention include nonionic, anionic or cationic compounds. Preferred surfactants are effective emulsifiers. As the concentration of the surfactant increases at or above the critical micellar concentration (CMC) value a micellar/bilayer emulsion is established. The emulsion can be configured with the resin in the hydrophobic phase as droplets and the reagent in the hydrophilic phase. The surfactant can also act as a surface wetting agent and a particle size-controlling agent (nanoscale) in a micelle matrix.

The reagent can dissociate in an aqueous solution to a hydronium ion and a conjugate anion in equilibrium. The reaction of hydronium ions and the paint components allow the dissociation to continue until the paint is hardened. When the metal salt containing the same conjugate anion as the dissociated reagent is added, the conjugate anions from the metal salt stabilize the reagent by stopping or reversing dissociation. This activity of the conjugated ions of the metal salt is

referred to as the common-ion effect. Also, the metal ion of the metal salt becomes associated with the phosphate layer and contributes to the inhibition of corrosion as a component of the layer.

Suitable amines for use in the coating of the present invention include, but are not limited to, primary, secondary or tertiary amines, preferably secondary or tertiary amines. Representative amines are alkyl amines, phenyl amines, aryl amines and substituted phenyl amines in general and, more specifically, triethylamine, diphenylamine, triphenylamine, the other similar compounds known to those of skill in the art, and mixtures thereof. The alkyl group preferably has 1 to about 6 carbon atoms. The weight ratio of the phosphatizing reagent to the amine is in the range of about 2:1 to about 1:1.5.

Representative resins include alkyd resins, acrylic resins, polyurethane resins, phenol formaldehyde resins, polyester resins, epoxy resins, and alkyl vinyl resins. The alkyl group of the alkyl vinyl resin preferably contains one to about five carbon atoms. Commercially available polyester resins are known to those of skill in the art.

Representative surfactants include oxyalkylated alkyl phenols such as Triton X-100, which is commercially available from Rohm & Haas and N-lauroylsarcosine and sodium dioctyl sulfosuccinate that are commercially available from American Cyanamid under the designation Aerosol OT (75%).

Metal ions and the conjugate anions of a metal salt can be obtained by utilizing zinc phosphate, iron phosphate, zinc iron phosphates, sodium metavanadate, ammonium cerium (IV) nitrate, zirconyl chloride hydrate, and zinc molybdate in the paint.

The solvent is preferably water miscible. Representative solvents include, but are not limited to, aliphatic alcohols, (e.g., isopropyl alcohol), butyl alcohol, aromatic and aliphatic hydrocarbons, glycol ethers, alkyl carbitols, (e.g., butyl carbitol), aromatic and aliphatic solvents, other similar solvents, and mixtures thereof. The alkyl groups preferably have one to about five carbon atoms.

Representative pigments include both organic and inorganic pigments, such as carbon black, titanium dioxide, Cu-phthalocyanine blue, Cu-phthalocyanine green, chrome yellow, iron oxide red, and the other pigments known to those of skill in the art.

5 In one embodiment, the paint contains the phosphatizing reagent in an amount in the range of about 0.5 to about 10, preferably about 0.5 to about 5 weight percent (wt %), the amine in an amount in the range of about 0.25 to about 15, preferably about 0.3 to about 7.5 wt %, the resin in an amount in the range of about 10 to about 70, preferably about 5 to about 15 wt %, the solvent in an amount in the range of about 0.5 to about 90 wt %, the surfactant in an amount in the range of about 0.1 to about 8 wt %, the metal salt in an amount in the range of about 0.5 to about 5 wt %, and pigment in an amount up to about 50 wt %, the wt %s being based upon the total weight of the paint. Preferably, the phosphatizing reagent is present in an amount in the range of about 2 to about 15 wt % based on the total weight of the solvent.

The paint preferably contains the metal chelating agent, organofunctional silanes, in an amount in the range of about 0.5 to about 10, preferably about 0.5 to about 3 weight percent (wt%) of the total paint formula weight. The paint also contains silicating agents, ion-exchanged silica gels, in an amount in the range of about 0 to about 20, preferably about 0.5 to about 5 weight percent (wt%) of the total paint formula weight.

Preferably, the additive package is produced prior to admixing with the coating composition or the resin. The phosphatizing reagent and amine are admixed to produce the reagent-amine complexes. The conditions under which the additive package is produced are preferably dispersion of the reagent and amine separately in a solvent at or near ambient conditions to produce a reagent solution and an amine solution. The reagent solution is then added slowly to the amine solution while mixing.

The ion-exchanged silica gels can be post-added in a fully formulated paint system or pre-added to resins. When a metal chelating is also added, the organofunctional silanes are preferably post-mixed to a fully formulated paint.

Preferably, one or more of the solvent, surfactant, and metal salt are also part of the additive package to further stabilize the reagent.

Alternatively, the additive package can be made in the paint by adding some or all of the components of the paint into a suitable vessel and mixing. The paint is
5 produced by admixing the components under ambient conditions for a time period effective to produce a homogeneous mixture.

Representative substrates to which the paint can be applied include, but are not limited to, metal, e.g., steel, cold-rolled and electrogalvanized steel, hot dipped galvanized, galvalume, copper, aluminum, magnesium, titanium, other metals, and
10 their alloys, wood, and thermoplastic and thermoset plastics.

In one preferred embodiment, the present invention provides and utilizes a silane dispersion technique in an *in-situ* phosphatizing paint that forms an organic and inorganic hybrid formulation. The organofunctional silanes can chelate metal active sites and thereby inactivate substrate corrosive sites. The organofunctional
15 silanes can provide a better pigment dispersion, and can act as coupling agent for a better polymer film. Preferably, the present invention provides and utilizes an ion-exchanged anti-corrosive pigment that generates a silicate layer for inhibiting corrosion *in situ*. Therefore, the present invention creates a better end product with the benefits disclosed above. In preferred embodiments the present invention
20 provides "nanoscale" and "green chemistry" approaches and therefore is safer both for the individual using the coating and the environment. The coating of the present invention does not contain chromates while maintaining the corrosion resistance properties of chromate-containing products.

More specifically, the additive package includes chemical ingredients that are
25 safe and which effectively replace prior art phosphate and chromate conversion coatings.

In preferred embodiments, the phosphatizing reagent includes the reaction product of an organic phosphate (or an organic phosphonate) with an amine. The organic phosphate and amine complex can combine more readily with other
30 components of the paint without excessive amounts of organic solvent as is required

when phosphoric acid is utilized. The volatile organic compound (VOC) content of the paint can be reduced as compared to a phosphoric acid-containing paint due to the reduction in the solvent needed. Further, the coating includes a more hydrophobic phosphate (or phosphonate), as compared to phosphoric acid, to avoid the problems associated with phosphoric acid in its free form. The end result being that the coated surface is protected and the disadvantages of phosphoric acid are avoided because phosphoric acid is not used.

The organic phosphate-amine (or organic phosphonate-amine) complexes can dissociate on the surface upon curing so that the free reagent is available to chemically and/or mechanically react *in situ* with the surface to form a phosphate layer.

Admixing the additive package with a polymer coat forming resin and a cross-linking agent produces the self-phosphatizing and silicating paint. Alternatively, the paint can be produced by admixing the additive package with a coating composition that includes the resin. If the coating composition does not include the cross-linking agent, one can be added. Due to the complexing of the acidic reagent with the amine, the paint can be pigmented without aggregation of the pigment.

A method of protecting the surface of the substrate includes the steps of applying the paint to the surface and forming a dry, protective coat from the paint on the surface.

The method of protecting the surface includes the steps of applying the paint to the surface and forming a dry protective coating on the surface. Preferably, the thickness of the paint applied to the substrate is in the range of about 0.04 millimeters (~1 micrometer) to about 3 millimeters so that most of the reagent can migrate to the surface, thereby minimizing the amount of reagent that remains in the coating after it dries.

The paint on the surface is dried using heat, UV light, or air-drying which dissociates the complexes, drives off the solvents, and contributes to the breakdown of the micelles if a surfactant is utilized. The net result is the formation of the phosphate and silicate layer, and the topcoat.

When heat is used, preferably the paint is cured at a temperature in the range of about 90° to about 700°F for a time period of about 10 seconds to about 30 minutes. The higher temperature requires a shorter curing time.

5 Paints utilizing the additive package are capable of inhibiting corrosion of the substrate in a single step application that is inherently better than a multi-step process because of the formation of the phosphate and silicate layer, the generation of dense and defect free paint film and the reduction in the number of steps in paint application.

10 The meticulous cleaning pretreatment of the metal surface that was required with the aforementioned multi-step processes is not necessary when the paint is utilized. Thus, a reduction in the number of defects that arise from improper cleaning pretreatment is obtained by utilizing the paint.

15 The coating of the present invention eliminates the need for the iron phosphatizing and the zinc phosphating processes and their baths that results in elimination of the tight chemical controls of the iron phosphate bath, the environmentally hazardous additives of the zinc phosphating process and the sludge production in the bath. The elimination of the sludge eliminates the defective surfaces due to sludge contamination being on the surface.

20 The problems of porosity and degradation associated with multi-step processes are also avoided, because the phosphate chemistry, silicon chemistry, and the polymer chemistry in the unicoat system proceed independently and simultaneously.

25 In a preferred embodiment, the additive package can be used in a single-coat, *in situ* self-phosphatizing and silicate paint that protects a surface of a substrate to which the paint is applied. The additive package preferably includes at least one phosphatizing reagent that also acts as a catalyst for the entire polymerization process. The additive package preferably includes at least one metal chelating organofunctional silane or an ion-exchanged silica gel.

In another preferred embodiment, the *in-situ* phosphatizing reagents (ISPRs) are used to replace or partially replace para-toluene sulfonic acid (p-TSA) as acid catalyst in polyester-melamine polymerization. Coatings made with the ISPRs offer the following benefits. First, ISPRs lead to a preferred co-condensation reaction and give a denser and lesser defects paint film. Second, ISPRs inhibit the overbake softening and provide a wider temperature range for thermal curing (particularly, in coil coating application). Third, ISPRs act in both phosphate chemistry and polymer chemistry, thus no residual ISPRs remain in paint films to cause side effect in paint film performance. Fourth, ISPRs prevent the "yellowing" problem observed commonly in polyester-melamine systems.

The invention is further described in detail by reference to the following experimental examples. These examples are provided for the purpose of illustration only, and are not intended to be limiting unless otherwise specified. Thus, the invention should in no way be construed as being limited to the following examples, but rather, should be construed to encompass any and all variations which become evident as a result of the teaching provided herein.

EXAMPLES

Example 1:

Demonstrations of ISPC technology in laboratory-made paints and proposed feasibility study of commercial ISPC formulations. Two representative examples of ISPCs formulated for laboratory-made paints (a water-reducible alkyd paint and a polyester-melamine paint) have been reported by Applicant. Yu, T.; Lin, C. T. *In-situ* phosphatizing coatings III: A water reducible alkyd baking enamel. *J. Coatings. Tech.* 1999, 71, 87-96. Whitten, M.C.; Lin, C.T. Coating performance of polyester-melamine enamels catalyzed by an in-situ phosphatizing reagent on aluminum. *Ind. Eng. Chem. Res.* 1999, 38, 3903-3910. The present experiments can study the feasibility of applying ISPC technology to three commercial paints: (1) Adheron's MIL-PRF-23377 Class N Primer for aircraft coatings, (2) Valspar's polyester primer

for high-performance Purlin coatings, and (3) Caterpillar's DTM polyurethane topcoat for original equipment manufacture (OEM) coatings.

5 The technological innovation in ISPCs is its one-step self-phosphatizing process. In this green coating technology, *in-situ* phosphatizing reagents (ISPRs), safer and non-carcinogenic chemicals, are selected and their optimal quantities are pre-dispersed in a desired paint system to form a stable and compatible one-pack coating formulation. A single coat of the *in situ* self-phosphating paint is applied to an untreated metal substrate. The phosphatizing reagents react *in situ* chemically
10 and/or physically with the metal surface to produce a metal phosphate layer. At the same time, covalent phosphorus-oxygen-carbon (P-O-C) linkages are formed with the polymer resin. The formation of a metal phosphate layer *in situ* essentially eliminates the need for a surface pretreatment step that normally employs a phosphating line or bath. The ISPRs' functional groups form chemical bonds with
15 the polymer resin; these bonds act to seal and minimize the porosity of the phosphated substrate. The use of chemical bonds to seal the pores of metal phosphate layers *in situ* acts to enhance coating adhesion and suppress metal corrosion without the need for final rinses containing carcinogenic chromates (Cr^{6+}). In addition, the ISPR catalyzes a preferred polymerization reaction via co-
20 condensation to form a thermally stable and defect-free paint film. The result is a highly cross-linked coating that is less permeable to water and electrolytes, and thus gives a superior protective barrier.

25 The laboratory-made ISPC paints have been applied to three types of metal substrates: (1) cold-rolled steel or CRS, (2) 2024 T3 aluminum alloy, and (3) Ti-6Al-4V titanium alloy. Representative results from tests performed with these paint systems are listed below, and support the proposed extension of applying the ISPC technology to formulate three chrome-free commercial paints.

30 *Formation of Metal Phosphate Layer In Situ.* Figure 2 shows refractive FTIR spectra of (a) the iron-phosphate layer on CRS, (b) the aluminum-phosphate layer on 2024 T3 Al alloy, and (c) the titanium-phosphate layer on Ti-6Al-4V titanium alloy. All three phosphate layers were generated by ISPRs at the coating/substrate

interface. The nature of the metal-phosphate bonds formed in ISPCs was shown to have an interaction of the acid-base type, $\text{P-O}^-\text{M}^{n+}$, rather than an interaction of the induced dipole P=O/metal complex type. Yu, T., Li, L.; Lin, C. T. Chemical affinity of in-situ phosphatizing reagents on cold-rolled steel. 1: *Phys. Chem.* 1995,99,7613-7620. The P-O stretching (ν_3) and O-P-O deformation (ν_4) vibration modes in PO_4^{3-} are clearly observed in Figure 2. The ν_3 absorption peaks are observed at 1195/1147/1105 cm^{-1} , 1230/1196/1166 cm^{-1} , and 1150/1054/1041 cm^{-1} for the Fe-phosphate spectrum (Figure 2a), the Al-phosphate spectrum (Figure 2b), and the Ti-phosphate spectrum (Figure 2c), respectively. On the other hand, the ν_4 absorption peaks are located at 564 cm^{-1} , 603/565 cm^{-1} , and 564/545 cm^{-1} for spectra shown in Figures 2a, 2b, and 2c, respectively. A spectral band (or a shoulder feature) at ~930-970 cm^{-1} is attributed to the formation of a covalent bond of P-O-C linkage between the metal phosphate layer and the polymer resin. The other peaks at 700-750 cm^{-1} in Figure 2 are from C-H out-of-plane and in-plane bending. Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. *Spectroscopic Identification of Organic Compounds*, 4th ed.; John Wiley and Sons, Inc: New York, 1981.

The frequency of the ν_3 absorption bands increases as the metal substrate changes in the following order, Al-phosphate > Fe-phosphate > Ti-phosphate. The observation can be attributed to a lower bond order in the P-O bond due to the lower ionicity of the Ti-O bond as compared to the Fe-O bond, which in turn has a lower ionicity than the Al-O bond. Neuder, H. A.; Sizemore, C. A.; Whitten, M. C.; Yu, T.; Lin, C. T. Surface adhesion in in-situ phosphatizing coatings. *J. Adhes. Sci. Technol.*, submitted for publication. Absorption bands recorded in Figure 2 give evidence that an *in-situ* phosphate layer has been produced on metal substrates. Furthermore, since the phosphate layer was not removed when the sample was rinsed with deionized water, acetone, and ethanol, the ISPR has clearly reacted and bonded with the metal surface.

Surface Adhesion of Paint Films. The salt-water immersion test is used to verify the surface adhesion of paint films. Coating adhesion to the metal substrate is particularly important for Ti alloys and Mg alloys. Titanium alloys such as Ti-6Al-4V

need a good organic coating to serve as an electrical insulation and interrupt the metal connectivity. In other words, a good coating of the Ti cathode is required.

Surface adhesion tests of paint films were conducted on several different metal substrates. In the tests, a laboratory-made polyester-melamine coating system catalyzed by *p*-TSA was used as control paint, and compared to an ISPC paint catalyzed by arylphosphonic acid as an ISPR. The control and ISPC paints were separately applied and cured on bare and chrome-treated (Alodine 1200) Ti alloy coupons. Figure 3 shows the results for the four painted Ti alloy coupons after six days of soaking in 3% NaCl solution. On the chromated panels, less than 0.5 mm was removed from either side of the "X" scribe for both the control paint (Figure 3C) and the ISPC paint (Figure 3D). The ISPC paint on bare titanium (Figure 3B) has approximately 1 mm of paint removed from the scribe, which is still considered a very good coating performance. The control paint on bare titanium (Figure 3A), however, shows complete failure, with virtually all paint removed from the scribed area. Obviously, the presence of the Ti-chromate layer improves the adhesion performance of the paints under these testing conditions. More importantly, the Ti-phosphate layer generated by ISPCs gives a comparable paint adhesion performance to that of the chromate treatment process. The ISPC system's primary chemical interaction at the coating's interface should provide greater resistance to wet adhesion loss than the control paint on bare Ti-6Al-4V substrates with only secondary interactions.

Corrosion Resistance of Metal Substrates. EIS has been proven to be a powerful tool for the determination of coating performance and underfilm metallic corrosion. Scully, J. R. Electrochemical impedance of organic-coated steel: Correlation of impedance parameters with long-term coating deterioration. 1: *Electrochem. Soc.* 1989, 136, 979-990. Control and ISPC paint formulations of polyester-melamine systems applied on untreated and chromated (Alodine 1200) 2024 T3 Al alloy coupons using this technique. Figure 4 shows the Bode-magnitude plot (log impedance vs. log frequency) after the painted panels were soaked in a 3% salt solution for 72 hours. All the impedance data are normalized to 1 cm² in units of $\Omega \cdot \text{cm}^2$. A paint film with an impedance value of 10⁹ $\Omega \cdot \text{cm}^2$ or higher at low

frequencies is considered a good protective barrier for the metal substrate. Leidheiser Jr., H. Towards a better understanding of corrosion beneath organic coatings. *Corrosion* 1983,39(5), 189-201. The ISPC paint (catalyzed by arylphosphonic acid, ISPR) shows very high impedance values at low frequencies ($> 10^{10} \Omega \cdot \text{cm}^2$ at 0.01 Hz) when painted on both the bare (curve b) and the chromated (curve a) aluminum panels. This demonstrates that the ISPC formulation provides a good protective barrier. The control paint (catalyzed by Cypat 4040, p-TSA) applied on chromated (curve c) and bare (curve d) Al coupons shows an impedance value below $10^7 \Omega \cdot \text{cm}^2$ at low frequencies, indicating a poor protective barrier. The use of the ISPR as the catalyst and *in-situ* phosphatizing reagent in the ISPC paint (curves a and b) increases the impedance at low frequencies by at least 10,000 times when compared to that of the control paint (curves c and d). Interestingly, curves a and b in Figure 4 show identical AC impedance behavior, indicating that the chromating process of 2024 T3 Al substrates is not required for the ISPC to achieve an excellent protective barrier. When the high-frequency portion of the Bode-magnitude plots in Figure 4 is examined, the ISPC painted on bare and chromated Al panels (curves a and b) has a slope of -1 , indicative of a pure capacitor. Since the impedance at the higher frequency portion of the Bode-magnitude plot is due to the organic coating itself, using the ISPR as the catalyst creates a denser and more uniform coating when compared to the control (curves c and d).

Figure 5 shows the final impedance data for all painted panels after soaking them in a 3% salt solution for 2500 hours. The impedance at low frequencies is lower for all the coupons when compared to their values after soaking for only 72 hours (Figure 4). The ISPC formulation (curve 5a) on the chromated Al panel has an impedance of almost $10^9 \Omega \cdot \text{cm}^2$, indicative of the maintenance of a good protective barrier. The ISPC formulation (curve 5b) on the bare Al panel has an impedance close to $10^8 \Omega \cdot \text{cm}^2$, indicating a mediocre barrier. A poor protective barrier is shown for the control paint on the chromated and the bare Al panels (curves 5c and 5d), where the impedance at low frequencies is on the order of $10^5 \Omega \cdot \text{cm}^2$.

The salt solution causes a loss of interfacial impedance in all the systems since the lower frequencies of the Bode-magnitude plot are attributed to the

electrochemical activities between the coating and the metal substrate. The high-frequency portion of the Bode-magnitude plot for the ISPC on both the chromated and bare Al panels (curves 5a and 5b) retains a slope of -1. Therefore, the polyester-melamine paint catalyzed with arylphosphonic acid (which also acts as an
5 *in-situ* phosphatizing reagent) still behaves as a capacitor even after 2,500 hours of exposure to a corroding salt media.

The testing conditions used in the standard salt (fog) spray tests for organic paint films are more aggressive and severe than those employed in the salt water
10 immersion tests described above. A slightly elevated temperature of 35 °C is combined with a continuous spray of salt solution. The airflow generated in the salt solution spray can carry fresh oxygen to the test chamber.

In the tests, coupons painted with water-reducible alkyd coating of about 1.0
15 mil (or 25 µm) dry film thickness (cured at 325 °F for 15 minutes) were first put through salt-water immersion tests and then X-cut to the substrate. The coupons were then subjected to a 100% humidity environment along with the 5% salt mist that serves as a conductive circuit for electrochemical reactions during the corrosion process. The test coupons were removed from the test chamber after 100 hours and
20 the coated surface was immediately dried. A Duck® brand tape was applied over the X-cut and then removed. The paint protective performance was assessed quantitatively by measuring the distance of the coating corrosion across the X-scribe.

Figure 6 shows the results of this 100-hour salt (fog) spray test for both
25 control (top three coupons) and ISPC (bottom three coupons) alkyd formulations. The coatings were painted on bare CRS (Figures 6 a and b), B-1000 (phosphated CRS, Figures 6c and d), and BD+P60 (phosphated and chromated CRS, Figures 6e and f). On all three types of substrates, the control alkyd paint provided much less corrosion protection, whereas less paint deterioration was found for the ISPC alkyd
30 formula. The ISPC water-reducible alkyd paint applied on bare CRS panel (a single-step *in-situ* phosphatizing coating, Figure 6b) out-performed the control alkyd paint on the pre-phosphated and -chromated substrate (a state-of-the-art multi-step

coating process, panel 6e), indicating a significant advantage of the single-step ISPC technique over the traditional multi-step surface pre-treatment/painting process.

Example 2:

340g/L VOC solvent borne non-chromate epoxy primer

5

Resin System Study.

Commercially available MIL-PRF-23377 primers are based on epoxy/polyamide chemistry. Epoxy/polyamide coatings give very good solvent and fluid resistance. The epoxy provides excellent corrosion protection and adhesion over marginally cleaned metal surfaces. Their shelf stability is much better than their waterborne counterparts. If the EPA exempts *tert-butyl* acetate (TBA) as a solvent in the near future and TBA is incorporated into the formulas, the VOC content of the primers can be further reduced. However, the surface dry time, film flexibility and impact resistance of epoxy/polyamide coatings are relatively poor. MIL-PRF-23377 specifications require primers to pass a 10% G.E. elongation test. A urethane topcoat meeting these specifications with 40% elongation is coated over the MIL-PRF-23377 primers. The elongation differential between primer and topcoat can understandably lead to early cohesion and inter-coat adhesion failure. Therefore, a more flexible primer (e.g., with elongation of 20% or greater, to minimize the different expansion and contraction coefficients) is needed to extend the service life of the entire coating system. The studies focus on polyamides with fewer primary and secondary amino groups to reduce the cross-linking density (T_g) of the films. Both aliphatic and oil-based mono-epoxy functional reactive diluents and their use levels in the formulas can be explored. When low functional polyamides and mono-functional diluents are employed in the formulas, the system suffers slower curing, which is undesirable for aerospace applications. To compensate for this potential problem, higher molecular weight epoxies and/or other amorphous polymers can be used. Such materials also provide additional adhesion to the epoxy systems.

Anti-Corrosion Studies.

Research efforts concentrate on newly developed and commercially available anti-corrosion pigments and/or organic polymers, and their synergistic effects on

corrosion protection. Electrochemical impedance spectroscopy (EIS) can be used to screen potential candidates followed by lengthy salt spray and filiform corrosion tests.

5 A prototype high solids (340g/L VOC max.) high performance chrome-free primer was recently developed in the lab, based on Adheron's proprietary anti-corrosion materials. The corrosion protection properties of this primer on 2024-T3 Clad Alodine 1200 treated panels are very promising. In fact, the primer passed a salt spray corrosion test of 2,500 hours. After 3,000 hours, less than one-half of one
10 percent of the total scribed area was found to have some white rusts (Figure 7). The rusted areas were no larger after 4,500 hours. No other film defects (such as blisters, pits, or film leave-off, etc.) were detected.

 All visual examinations were aided by using a 10X magnifying glass. Testing
15 substrates (such as 2024-T3 / Clad Alodine 1000, 2024-T3 / Bare Alodine 1200, and 7075-T6 / Alodine 1200) is currently underway in the laboratory and Boeing Commercial Aircraft Group's laboratory in Seattle. Feedback based on preliminary salt spray results from Boeing is very positive, but additional studies are needed. The primer is compatible with MIL-PRF-85285 urethane topcoats.

20

 Another area of focus is the selection of fillers, which also play an important role in corrosion protection. A tightly packed film made of fillers with different geometric shapes can slow down the diffusion rates of moisture to the metal substrate surfaces. Thus an extended protection period can be expected for the
25 primer. Preference in selection of fillers can be given to ones with lower specific gravities in order to reduce the weight of the primers on the aircraft. The preferred system should have a lower density.

Surface Appearance and Application Parameters.

30

 Epoxy/polyamide systems tend to produce films with defects such as orange peels. Surface defects like this can be carried over (or transferred) to the topcoats. Thus, the topcoat's appearance (and possibly performance) can be less than perfect.

The systems also show gloss variations especially when the admixture is used during the later pot life period. Therefore, flow and rheology additives, pigment/filler oil absorption, resin viscosities, and solvent combination are all important factors to be considered.

5

All coatings designed for field application should ideally be error proof. Coatings with longer usable pot life, tolerance in mixing ratios, low application viscosities, and fast drying at ambient temperatures are very desirable.

10 ***Stable and compatible ISPC/ChemNova/AC***

Current pretreatments on aluminum alloys for aircraft include chromate conversion coatings such as Alodine 1000 and 1200. The conversion coatings contain Cr^{+6} , which is toxic and carcinogenic. Coating films are brittle, which can
15 cause coating adhesion failure around rivets, fasteners, and seams when the fuselage expands and contracts. In addition, the conversion coatings can never completely cover the imperfect alloy surfaces. In contrast, the ISPC technology produces a metal phosphate layer, which is effectively sealed by P-O-C linkages, that forms an intimate contact over the metal substrate that has been verified in
20 laboratory tests. Therefore, superior adhesion, flexibility, and corrosion can be expected from ISPC applications.

ISPC formulation chemistry can be thoroughly studied. ISPRs can be selected from the derivatives of arylphosphonic acids and arylphosphoric acids. These
25 organic phosphorus compounds are easily dispersible in paint formulations. The optimal amount of desired ISPRs can be dispersed in the epoxy component of the primer. The storage stability and rheological profile of the ISPC formulation is similar to that of the control sample for component A. The ISPC formulation meets all the requirements specified herein after storage for a period of one year where the daily
30 ambient air temperature is maintained at 1.7-46 °C. The degree and rate of in-can reactions, due to the dispersion of ISPRs, were monitored by a computer automated rheology viscometer at regular intervals. Apart from the changes in physical

properties, the system stability of ISPCs can also be probed for chemical transformation by using FTIR spectroscopy.

Sol-gel coating catalyzed by ISPRs on 2024 T3 alloy (sol-gel / ISPR/asp)

5

A Tri-Service/DOE Strategic Environmental Research and Development Program (SERDP) effort, entitled "Sol-Gel Technology for Low-VOC, Non-Chromated Adhesive and Sealant Applications," began in 1998. The use of mono- and bi-silanes for corrosion control of metals and bonding of silane-treated metals to paint systems and rubber compounds has been reported. Recently, an epoxide-modified silicate sol-gel film spray-coated on an aluminum alloy demonstrated good barrier and corrosion control properties when compared to chromate-based surface treatments. However, the results to date indicate that current state-of-the-art non-chromated coating systems are significantly less effective than those with chromate. The sol-gel coating systems used in these investigations are all catalyzed by acetic acid, and the sol-gel films thus obtained are porous and water-sensitive.

As has been described above, the ISPC technology works because the selected ISPRs are designed both to provide generation of *in-situ* metal phosphatization and simultaneous catalysis of polymer curing reactions. The present invention provides sol-gel coatings catalyzed by *in-situ* phosphatizing reagents, instead of acetic acid. The advantage of using an ISPR is that it avoids the problem of residual acetic acid (or acetate) entrapped in the sol-gel matrix, causing corrosion or paint delamination effects. The residual ISPR (or phosphate), in contrast, can react with the metal surface to form metal-phosphate bonds that would aid in sealing the pores of the sol-gel network and enhance the coating performance.

Verification of Chrome-Free Pretreatment and Primer for Aerospace

The chrome-free epoxy primer (ChemNova/AC) and ISPC epoxy primer (ISPC/ChemNova/AC) developed in this invention can be applied to chrome-free untreated 2024-T3 and 7075-T6 Al substrates, and also to 2024 T3 and 7075 T6 Al substrates treated by an ISPR-catalyzed, chrome-free sol-gel (sol-gel/ISPR/asp)

system. The electrochemical impedance spectroscopy (EIS) technique established in the lab can be utilized to study the deterioration of paint films and under-film corrosion attack. Electrical equivalent circuit models that simulate the interface between the metal and the phosphate layer (or metal oxide layer), and between the coating and an attacking electrolyte can aid in the analysis of the EIS data obtained.

"Real world" tests, including salt (fog) spray (ASTM B-117), have been verified.

10 *Some Illustrations of ISPCs Related to this Project*

FTIR of the aluminum-phosphate product generated in ISPCs. Figure 8 shows the 80° grazing angle FTIR reflectance spectrum of the ISPR-generated metal-phosphate layer on polished 3003 Al. The peaks at 1230/1196/1166 cm^{-1} are attributed to the P=O absorption band or ν_3 vibration mode in PO_4^{3-} . The peaks at 603/565 cm^{-1} are due to O-P-O absorption bands or ν_4 vibration mode in PO_4^{3-} . The other peaks are from C-H out-of-plane and in-plane bending. A covalent bond of P-O-C linkages is evidenced at 934 cm^{-1} , which shows a strong coating adhesion at the polymer paint film/metal phosphate interface.

20 *Morphology of aluminum-phosphate product generated in ISPCs.*

The photographs in Figure 9 are magnified 5X and were taken under an optical microscope. Some photographs also have photographs at 80X magnification inserted in the main photo for additional detail. Figure 9A shows bare polished Al, having a clear texture. Figure 9B shows that ISPR-2 produced a metal-phosphate product with good adhesion to the surface, but the layer appears to be very thin since the base metal can still easily be seen underneath. Furthermore, there is cracking in the surface. ISPR-I shows a very nice uniform covering of the Al surface in Figure 9C. The uniformity is confirmed in the 80X magnification inserted in the 5X photo. The base metal is not visible on the surface of the sample. The metal-phosphate product generated by reacting Albright & Wilson PA-75 on the surface of Al appears to show uniform coverage when magnified at 5X (Figure 9D). However,

upon closer inspection at a magnification of 80X, it is clear that the coverage isn't as uniform as ISPR-1 (Figure 9C). The metal-phosphate layer produced by reacting Cypat 296-9 on the surface of Al does not cover the surface uniformly (Figure 9E). The phosphate layers appear to grow in islands. The quantitative analysis of the surface was conducted with EDX. ISPR-I, which shows uniform coverage in optical microscopy, shows the same result in EDX, with 20 weight percent of P on the surface of the sample.

EIS results of ISPC polyester-melamine on 2024 T3 aluminum coupons.

10

Figure 4 shows a Bode-magnitude plot after painted panels were soaked in a 3% salt solution for 3 days- The ISPC polyester-melamine paint system, which is catalyzed with 1.5% ISPR, shows very high impedance value at low frequencies ($> 10^{10}$ ohm cm^2 at 0.01 Hz) when painted on both the bare (curve b) and the chromated (Alodine solution-MIL-C-5541, curve a) aluminum panels. The control paint, catalyzed with Cypat 4040, produced a value below 10^7 ohm cm^2 at low frequencies on chromated (curve c) and bare (curve d) Al. The ISPR catalyst in the ISPC formulation increases the low-frequency impedance on curves a and b by at least 10,000 times over the control. Moreover, curves a and b show identical AC impedance behavior, indicating that the chromation of 2024-T3 Al substrates is not required for the ISPC to achieve an excellent protective barrier.

20

Adhesion test.

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The painted Al coupons and paint samples are the same as Figure 4. A pressure-sensitive tape is placed on the area of the painted EIS sample panels exposed to the salt solution after 102 days and removed. The results are shown in Figure 10. Both the bare (Figure 10A) and the chromated (Figure 10B). Al panels painted with the control paint show extremely poor adhesion, suggesting that the chromated layer no longer retains its adhesive abilities after saturation with the salt solution. The ISPC paint is displayed in Figure 10C (bare Al) and D (chromated Al). The tape removes a very tiny spot of paint from the bare Al panel painted with the

30

ISPC, but there is no paint removal on the chromated Al panel painted with the ISPC.

Example 3:

5

Materials and technical data

A high-solids solvent-borne non-chromate epoxy primers (e.g., CD112) was formulated. . The CD112 system has a mixing ratio of 3 to 1 by volume of epoxy to polyamide, and contains 340 g/L VOCs (volatile organic compounds, determined by
10 ASTM D2369). The solids content by weight is $73.0 \pm 1.0\%$. Great care was taken to control the molecular factors, including the functional reactive diluents of epoxy, the primary and secondary amino groups of polyamide, anti-corrosive pigments, and the geometric shapes of fillers. The chrome-free emulsion for surface pretreatment of
15 aluminum alloys contains about 20% by weight of acrylic co-polymers. Since the desired thickness of a surface pretreated dry film is on the order of $1\mu\text{m}$, the formulation design is focused on the selection of nanometer ($\sim 60\text{ nm}$) resin particle size, active metal chelating agents, anti-corrosive pigments with charge-transfer characteristics, and reactive organofunctional silanes. In preparing the ISPC⁵⁻¹³
20 chrome-free epoxy primer, two effective ISPRs were selected: functionalized arylphosphoric acid (referred to as ISPR -1) and functionalized arylphosphonic acid (referred to as ISPR-2). The ISPR was dispersed directly into the paint formulation by a high-speed mixer, or dissolved in a suitable solvent mixture first and then mixed with paint system. The amount of ISPR used is in the order of 1-2% by weight of
25 ISPR to the total weight of paint formulation.

Instrumentation

AC impedance data for MIL-PRF-23377 epoxy primer coated on Al panels
30 were obtained using a PARC 273 potentiostat/galvanostat and a PARC 5210 lock-in amplifier (EG&G Princeton Applied Research). The experimental parameters were input and the data were collected with the aid of EG&G electrochemistry Powersuite

version 2.20 installed on a DELL PC 8100 computer. An Ag/AgCl electrode was used for the reference, a platinum electrode was used for the counter, and the coated panel was the working electrode. The coated panel had an area of 10.0 cm² exposed to the salt solution. The electrolyte used was a 3% NaCl aqueous solution.

5 The impedance measurements were carried out over the frequency range 100 kHz-10 mHz with a 20 mV peak-to-peak sinusoidal voltage. The impedance data were taken after the coated panels had been soaked for 72, 500, and 1000 hours in a 3% NaCl solution.

10 The FTIR reflectance spectrum of the metal-phosphate layer on polished metal surface generated by the ISPR was taken with a Broker Vector 22 equipped with a Spectra Tech FT-80 grazing angle accessory. The FTIR spectrometer was controlled by a computer program, OPUS/IR version 2.2. The microscope photos of metal phosphate layer were acquired with a Nikon Microphot-FXA equipped with a
15 Polaroid model 545 4x5 film holder. Scanning electron microscopy (SEM) was carried out with an ISI Model DS-130 (International Scientific Instrumentation, Inc.) and energy-dispersive X-ray spectroscopy (EDX) with a PV9900 system (North American Philips Company).

20 Salt (fog) spray analysis was done using a 5% NaCl solution. The coated panels had an "X" scribed on the painted panels and were exposed for 1000, 2000, and 3000 hours as per ASTM method B117. Paint and coating testing manual 14th edition of the Gardner-Sward handbook; Koleske, J.V. Eds.; ASTM manual series: MNL 17, ASTM PCN 28-017095-14: Philadelphia, PA, 1995. The "X" had a 0.1 mm
25 width and sufficient depth to remove the pretreatment Alodine 1000, Alodine 1200, and chrome-free acrylic emulsion (AFP), and completely exposes the bare alloy. A 10x magnifying lens was used to examine the test panels.

Results and Discussion

30

A 340 g/L vac solvent-borne non-chromate epoxy primer (CD112)

The CD112 primer is a chrome-free epoxy primer designed for aerospace applications. It provides excellent corrosion, solvent, chemical, and fluid (including Skydrol¹⁵) resistance. It is compatible with high-solids urethane topcoats. (MIL-PRF-85285C Type 1, DOD Performance Specification (US Navy), and Coating: Polyurethane, High-Solids.) Paint film adhesion, both when wet and dry, is excellent. Salt spray tests (Koleske) and filiform corrosion tests (filiform test involves a primer and polyurethane topcoat system. The total system is scribed and subjected to 60 seconds in conc. HCl vapor and then immediately placing it in a chamber with 80% RH and 104 °F for 1000 hours. After the test, the painted panel shall not exhibit filiform corrosion extended beyond 1/4" from the scribe. A test was conducted for CD112 primer using MIL-PRF-23377² type 1 approved chromate-based primer, AD9318/AD2298, from Adheron Coating Corporation (Oak Forest, IL) as a control. Tests were carried out on three aluminum alloys: 2024-T3 Bare/Alodine 1200, 2024-T3 Clad/Alodine 1000, and 7075-T6 Bare/Alodine 1200. A 0.8-0.9 ml dry film was prepared and cured for 14 days at ambient temperature before testing. Table 1 summarizes the salt spray testing results (1040 hours, 2022 hours, and 3004 hours) of both the CD 112 non-chromate primer and the AD9318/ AD2298 chromate primer on all three aluminum alloys. For visual inspection, the photographs of 3004-hour salt spray testing panels are displayed in Figure 11.

No testing panels showed any field blisters, white pits, or other undesirable defects. The CD112 non-chromate primer gives 3000-hour salt spray resistance compatible to its chromate counterpart (AD9318/AD2298) on both 2024-T3 Clad/Alodine 1000 (third row of Table 1, and pictures C and D of Figure 11) and 7075-T6 Bare/Alodine 1200 (fourth row of Table 1, and pictures E and F of Figure 11). The CD 112 system passes a 1000-hour salt spray test on 2024-T3 Bare/Alodine 1200, and less than 20% of the scribe area showed white rust after a 3000-hour salt spray test. Both the CD112 non-chromate primer and the AD9318/AD2298 chromate primer pass a 1000-hour filiform corrosion test. This filiform corrosion test was performed on a complete system where a high solids polyurethane topcoat (Paint and coating testing manual 14th edition of the Gardner-Sward handbook; Koleske, J. V. Eds.; ASTM manual series: MNL 17, ASTM PCN 28-017095-14: Philadelphia, PA, 1995.) was applied over the primer.

Table 1. Salt Spray Test Results for Non-Chromate (CD112) and Chromate Epoxy Primer

Substrate	Non-Chromate (CD112)			Chromate (AD9318/AD2298)		
	<u>Hours Exposure</u>			<u>Hours Exposure</u>		
	1040 h	2022 h	3004 h	1040 h	2022 h	3004 h
2024-T3 Bare/ Alodine 1200	NR S < 5%	R < 10% S < 10%	R < 20% S < 20%	NR S < 5%	NR S < 5%	NR S < 5%
2024-T3 Clad/ Alodine 1000	NR S < 5%	NR S < 5%	NR S < 5%	NR NS	NR S < 5%	NR S < 5%
7075-T6 Bare/ Alodine 1200	NR S < 5%	NR S < 5%	NR S < 5%	NR NS	NR S < 5%	NR S < 25%

NR: no white rust, NS: no stain

R: white rust, % scribe area

S: stain, % scribe area; it is not considered as defect.

A chrome-free acrylic emulsion for metal surface pretreatment (AFP)

- 15 The AFP (anti-fingerprint coating) was developed recently in the lab. It has been shown to provide excellent metal surface pretreatment on bare cold-rolled steel (CRS), galvanized steel, magnesium alloys, and titanium alloys. Here, the AFP system is extended and applied to the untreated 2024-T3 Bare Al coupon, by dipping and spinning off the excess emulsion. The pretreated Al coupon is then
- 20 thermally cured at 150°C (oven temperature) for 1 minute to give a treated 2024-T3 Bare/AFP Al panel. A 0.8-0.9 ml dry film of AD9318/AD2298 chromate primer was prepared on 2024-T3 Bare/AFP and 2024-T3 Bare/Alodine 1200 coupons, and cured overnight at 49°C. The resistance to corrosion of AFP and Alodine 1200 surface pretreatment on 2024-T3 Bare aluminum alloy is examined by salt spray tests (Paint
- 25 and coating testing manual 14th edition of the Gardner-Sward handbook; Koleske, J. V. Eds.; ASTM manual series: MNL 17, ASTM PCN 28-017095-14: Philadelphia, PA, 1995.) and EIS scans.

- 30 Figure 12 displays panels of 2024-T3 Bare/Alodine 1200 (Figure 12A) and on 2024-T3 Bare/AFP (Figure 12B) coated with AD9318/AD2298 primer after a 1000-hour salt spray test. Both panels are free of white rust, field blisters, white pits, or other undesirable defects. Figure 12A (Alodine 1200 panel) shows a few stains along the X-scribe area (similar to that listed in the second row and third column of

Table 1). Figure 12B (AFP panel) is free of stain. A slight decoloration (i.e., a leaching of chromate anti-corrosive pigments) is observed in Figure 12A, but not in Figure 12B. The non-chromate AFP surface pretreatment retains the chromate anti-corrosive pigments in the primer, while the Alodine 1200 pretreatment does not. The ability of AFP to retain the chromate pigments in the primer film can prolong the effect of corrosion resistance and, more importantly, can reduce the possibility of chromate contaminations of the groundwater and environment.

The salt spray testing results are in good agreement with the EIS measurements. Figure 13 shows the Bode-magnitude plots (frequency vs. impedance) of AD9318/AD2298 coated on 2024-T3 Bare/AFP panels after soaking in 3% NaCl solution for 72 hours (♦) and 1000 hours (▲), and those on 2024-T3 Bare/Alodine 1200 panels soaked for 72 hours (●) and 1000 hours (■). The paint film of AD9318 / AD2298 coated on 2024-T3 Bare AFP panel has a slope of nearly -1, indicating to a pure capacitor, with a high impedance value of 4×10^9 ohm.cm² at 0.01 Hz. This high quality of paint film protective performance is completely retained after soaking in 3% NaCl solution for 1000 hours (▲). On the other hand, the paint film of AD9318 / AD2298 coated on 2024-T3 Bare Alodine 1200 panel shows some stains in the salt spray test (Figure 12A) and thus gives a low impedance value of 4×10^7 ohm.cm² (●) which is 100 times lower than the painted AFP panel. A reduction in impedance value is also observed for the painted Alodine 1200 panel after soaking in 3% NaCl solution for 1000 hours (■).

An ISPC formulation of the CD 112 primer

Chrome-free single-step ISPC was developed recently. In an ISPC, an effective *in-situ* phosphatizing reagent (ISPR) is selected and its optimal amount is pre-dispersed in the paint system to form a stable and compatible one-pack coating formulation. When the ISPC is applied to a bare metal substrate, the ISPR reacts chemically and/or physically *in-situ* with the metal surface to produce an insulating layer of metal phosphate and simultaneously forms covalent phosphorus-oxygen-carbon (P-O-C) linkages with the polymer resin. The formation of a metal phosphate layer *in-situ* essentially eliminates the need for a phosphating line/bath. The

functional groups of ISPRs form chemical bonds with polymer resin that act to seal and minimize the porosity of the *in-situ* phosphated substrate. The use of chemical bonds to seal the pores of metal phosphate layer *in-situ* act to enhance coating adhesion and suppress metal corrosion without the need for post-treatment final
5 rinses containing carcinogenic chromates (Cr^{6+}). In addition, the ISPR catalyzes a preferred polymerization reaction via co-condensation to form a thermally stable and defect-free paint film. This highly crosslinked coating is less permeable to water and electrolytes, and thus gives a superior protective barrier.

10 The formation chemistry of metal phosphate layer in ISPCs (applied to a polyester-melamine system) is illustrated for two *in-situ* phosphatizing reagents. Figure 2 shows the FTIR spectra of (Figure 2a) iron-phosphate layer on CRS, (Figure 2b) aluminum-phosphate layer on 2024-T3 Bare Al alloy, and (Figure 2c) titanium-phosphate layer on Ti-6Al-4V titanium alloy generated by ISPR-2 (the
15 functionalized arylphosphonic acid) at the coating/substrate interface. The nature of the metal phosphate bonds produced in ISPCs was shown to have an acid-base type interaction, $\text{P-O}^- \text{M}^{n+}$, rather than an induced dipole interaction of the P=O /metal complex type. The P-O stretching (ν_3) and O-P-O deformation (ν_4) vibration modes in PO_4^{3-} are clearly observed in Figure 2. The ν_3 absorption peaks are observed at
20 1195/1147/1105 cm^{-1} , 1230/1196/1166 cm^{-1} and 1150/1054/1041 cm^{-1} , for the Fe-phosphate (spectrum shown in Figure 2a), Al-phosphate (spectrum shown in Figure 2b), and Ti-phosphate (spectrum shown in Figure 2c), respectively. The ν_4 absorption peaks are located at 564 cm^{-1} , 603/565 cm^{-1} , and 564/545 cm^{-1} , for spectra shown in Figure 2a, 2b, and 2c, respectively. A spectral band (or a shoulder
25 feature) at ~930-970 cm^{-1} is attributed to the formation of a covalent P-O-C linkage between the metal phosphate layer and the polymer resin. The other peaks at 700-750 cm^{-1} in Figure 2 are from C-H out-of-plane and in-plane bending. It is important to note that the frequency of the ν_3 absorption bands increases as the metal substrate changes (Al-phosphate > Fe-phosphate > Ti-phosphate). This observation
30 can be attributed to a lower bond order of the P-O bond due to the lower ionicity of the Ti-O bond as compared to the Fe-O bond, which in turn has a lower ionicity than the Al-O bond. Absorption bands recorded in Figure 2 give evidence that an *in-situ* phosphate layer has been produced on metal substrates. Furthermore, since the

phosphate layer cannot be washed off when the sample was soaked (and rinsed) with deionized water, acetone, and ethanol, the ISPR has reacted and bonded with the metal surface.

5 SEM (and optical microscope) and EDX were used to examine the morphology and chemical composition of metal phosphate layer generated on CRS, 2024-T3 Bare Al alloy and Ti-6Al-4V titanium alloy. It is observed that ISPR-1 (the functionalized arylphosphoric acid) and ISPR-2 react differently with metal substrates and form different surface structures of metal phosphates (not shown). For example, 10 ISPR-2 gives a uniform formation of a Fe-phosphate thin layer on the CRS substrate surface with almost 100% coverage (Figure 14a). For ISPR-1, the formation of a localized growth (island type) of Fe-phosphate structure is observed in the SEM scan (Figure 14b), and confirmed by the EDX spectrum (Figure 14d, the phosphorus peak observed at 2.02 keV). The key factor is the formation of a uniform metal phosphate 15 coverage over the substrate surface that is essential for providing a strong paint adhesion and superior corrosion resistance of metal substrates. Since ISPR-1 can only provide a localized "island shape" metal phosphate protection, ISPR-2, which shows much more uniform metal phosphate products, should be preferred as an ISPR in the formulation of ISPCs.

20 Two ISPC aerospace primers have been formulated that use the non-chromate CD112 primer described above, and two ISPRs (ISPR-1, the functionalized arylphosphoric acid and ISPR-2, the functionalized arylphosphonic acid). A 0.8-0.9 mil dry film was prepared for the non-chromate CD 112 primer on 2024-T3 25 Bare/Alodine 1200 (panel 1), ISPC/CD 112/ISPR-1 on 2024-T3 Bare (panel 2), and ISPC/CD 112/ISPR-2 on 2024-T3 Bare aluminum alloy (panel 3), and cured overnight at 49 °C. The panels were soaked in a 3% NaCl solution for 1000 hours before the EIS measurement was conducted to record both Bode and Nyquist plots. For a better representation, Figure 15 shows the Nyquist plots (Z_{im} -complex component of impedance vs. Z_{re} -real component of impedance) for panel 1, panel 2, 30 and panel 3. The Nyquist plot is generally characterized by a semi-cycle, and has a radius of $R_c/2$, where R_c is the coating resistance. The size of semi-cycle in Figure 15 follows the order of ISPC/CD 112/ISPR-2 ($R_c = 8 \times 10^7 \Omega \text{ cm}^2$) >

ISPC/CD112/ISPR-1 ($R_c=3 \times 10^7 \Omega \text{ cm}^2$) > CD112/2024-T3 Bare/Alodine 1200 ($R_c = 2 \times 10^7 \Omega \text{ cm}^2$). Both ISPCs on untreated 2024 T3 bare Al panels gave higher coating resistance than the control CD112 primer on Alodine 1200 treated 2024-T3 bare Al panel, indicating the *in-situ* metal phosphatization generated in ISPCs enhances the surface corrosive protection. The ISPR-2 produces more uniform metal phosphate products, so ISPC/CD 112/ISPR-2 has a higher R_c than ISPC/CD 112/ISPR-1, since ISPR-1 gives only the "localized island shape" metal phosphate protection.

10 Conclusions

A 340 g/L VOC solvent-borne non-chromate epoxy primer for aerospace applications (CD112) has been demonstrated. Based on salt spray and filiform corrosion test results, this system gives comparable anti-corrosion properties as its chromate counterpart on 2024-T3 Clad/Alodine 1000 and 7075-T6 Bare/Alodine 1200 aluminum alloys, but not as good for 2024-T3 Bare/Alodine 1200. A chrome-free acrylic emulsion was developed initially for the anti-fingerprint (AFP) coating of galvanized sheet steel. This AFP formulation is shown also as an excellent surface pretreatment system for 2024-T3 Bare aluminum alloy. Both salt spray test results and EIS measurements indicate that the AFP formulation can be adapted to replace Alodine 1200 for the surface pretreatment of 2024-T3 Bare aluminum alloy. More importantly, the AFP formulation works better than Alodine 1200 to reduce the "leaching" of chromate pigments contained in dry film of epoxy primers. The *in-situ* phosphatizing coatings (ISPCs) based on CD 112 aerospace primer are formulated for the first time. The ISPR-2 (the functionalized arylphosphonic acid) is shown to produce uniform metal phosphate products *in-situ* on substrate surface. A good protective performance is demonstrated for ISPC/CD112/ISPR-2 system that combines surface pre-treatment and primer into a single-step application.

0 Example 4

The *in-situ* phosphatizing reagents (ISPRs) described in this example was used to replace para-toluene sulfonic acid (p-TSA) used currently in the market

Catalysis of polyester-melamine paints usually requires the presence of an organic acid, such as para-toluene sulfonic acid (p-TSA). However, the p-TSA catalyzed paints suffer an overbake softening problem at high temperature curing schedule due to the breakdown of co-condensation reaction and the initiation of self-condensation. Thus, the paint films cured at a higher temperature have become more liquid-like and shown to reduce their protective performance. Using p-TSA acid catalyst is required to control the narrow window of thermal curing schedule. Since the ISPRs employed in this invention is acidic, its presence also aids in catalyzing the polymer crosslinking reaction. Using ISPRs invented, the overbake softening is not observed. In coating practice such as in coil coating, a wider range of curing temperature is available to maintain the good protective performance. These results¹⁰ are listed in Table 2.

Table 2. T_g and T_g Span of the Six Different Polyester-Melamine Paint System

% catalyst	T_g (scan 1)	T_g span (1)	T_g (scan 2)	T_g span (2)
1% ISPR	22.2	16.5	64.5	34.7
2% ISPR	37.5	23.3	53.6	48.2
3% ISPR	41.5	31.0	34.7	26.8
1% p-TSA	39.5	26.0	33.9	25.8
2% p-TSA	34.3	25.2	21.5	23.9
3% p-TSA	41.1	28.7	20.3	16.8

More interesting results are given under the headings " T_g (scan 2)" and T_g span (2)". These values are obtained when the same samples which were used to determine T_g (scan 1)" and T_g span (1) are rescanned to temperature of 300 °C (a simulation of overbake condition). It is noted that the T_g increases in the paints with 1% and 2% ISPR as the catalyst. This means that upon severe heating of the coating the average molecular weight of the polymers increased. The T_g value is generally related to the cross-linking density of a paint film, and thus correlated to the molecular weight of the resultant polymer film. In the 1% ISPR coating, the T_g increased from 22.2 to 64.9 °C, and from 37.5 to 53.6 °C in the 2% ISPR coating. In the 3% ISPR paint formula, the T_g decreases from 41.5 to 34.7 °C, indicating that 3%

ISPR is enough catalyst to end the trend of an increased T_g after exposure to high heat. The observed thermal trends using the various percentages of ISPRs as the catalyst were reproducible.

5 The T_g in the p-TSA-catalyzed paint systems decreases in all the paint systems, as seen in Table 2 (1% p-TSA [39.5 \rightarrow 33.9 $^{\circ}$ C], 2% p-TSA [34.3 \rightarrow 21.5 $^{\circ}$ C], 3% p-TSA [41.1 \rightarrow 20.3 $^{\circ}$ C]) A decrease in the T_g temperature upon heating shows that thermal decomposition occurred with the use of p-TSA as the catalyst since the average molecular weight of the polymer decreased. The greater thermal
10 decomposition or the forming of smaller molecular weight segments of the paints with p-TSA as the catalyst was confirmed using TGA as shown in Figure 16. On the average, the cured paints with the ISPR as the catalyst maintain approximately 94% of their weight when brought to 300 $^{\circ}$ C. The p-TSA-catalyzed paints maintain approximately 90% of their original weight. The ISPR catalyzed paint is thermally
15 stable. More thermal decomposition occurs when using p-TSA as the catalyst.

Six different phosphorus containing reagents were used as self-phosphating agent and acid catalyst in the formulation of a polyester-melamine coating.²¹ The results for all the paint catalyst used in this investigation are shown in Table 3.

20

Table 3 Paint Catalyst Used in Study

Catalyst	EIS (ohms-cm ²)	Tg($^{\circ}$ C)[after 300 $^{\circ}$ C]	Salt Water	Pencil
		Hardness		
1% 4040	10 ⁶	40[34]	1A	F
2% 296-9	10 ⁷	2.5[46]	N/A	4B

	2% 296-9* [†]	10 ⁹	21[52]	N/A	F
	1.3% PA-75	10 ¹⁰ & 10 ⁸	31[46]	4A	3H
	1% PA-75*	10 ¹⁰	23[56]	N/A	H
	1% PPSA	10 ⁶	24[53]	N/A	H
5	1% ISPR-1*	10 ¹⁰	22[65]	5A	F
	1% ISPR-2	10 ⁹ & 10 ⁷	35[59]	N/A	4H
	0.75% ISPR-2	10 ⁹	34[55]	N/A	4H
	0.5% ISPR-2*	10 ⁹	18[48]	5A	HB

*Paint systems used in further comparisons

10 [†]cured at 140°C

N/A not applicable, see text for further information

The data for 1% 4040 (p-TSA) catalyzed paint is listed in the first row. After painted panels had soaked in a 3% NaCl solution for 3 days, the impedance at low frequency (0.01 Hz) from EIS was on the order of 10⁶ ohms·cm². A surface with an impedance at low frequency below 10⁷ ohms·cm² is considered a poor protective barrier. Therefore, using 1% p-TSA as the acid modifier did not produce a cured polyester-melamine coating that was very resistant to the uptake of the salt solution. The T_g from the first DSC scan was 40 °C. After the paint was reheated to 300 °C for the second time, the T_g dropped to 34 °C, which indicated overbake softening behavior. A higher T_g correlates with a coating with a higher crosslinking density in the polymer. The crosslinking density dropped as the T_g dropped after severe heating. This resulted from the possible cleavage of polyester-melamine crosslinking in favor of the melamine self-condensation in the paint films. After one week of being submerged in a 3% NaCl solution, Duck brand tape was applied to the scribed area of the panel and removed. There was no adherence of the paint to the bare Al upon removal of the tape. The paint was classified as 1A according to ASTM method D3359 test method A. The pencil hardness was F.

When 1.3% PA-75 used as the acid additive in the polyester-melamine coating, a coating was produced that could not reproducibly show the same impedance at low frequency as shown in the fourth row of Table 3. Impedances on the order of 10^{10} ohms \cdot cm² and 10^8 ohms \cdot cm² at low frequency were measured. A difference of 2 orders of magnitude was concerning for painted panels that ideally should be identical. From DSC, the Tg was 31 °C the first time the sample was brought to 300 °C. The Tg increased to 46 °C during the second DSC run. Therefore, the cross-linking density of the polyester-melamine polymer increased after being subjected to an infinity curing. Painted panels that were soaked in a 3% NaCl solution for 66 days showed a uniform paint removal along the scribe of approximately 1 mm, which was evaluated as 4A by ASTM method D3359 test method A. There were no blisters visible on or discoloration of the paint after soaking the painted panels in the salt solution. The paint had a pencil hardness of 3H. The poor reproducibility shown in the studies using EIS possibly were due to the hardness of the paint. Perhaps, the brittleness of the paint caused the uniformity of the paint to be less, causing the paint resistance to decrease in areas where the paint cracked or had defects slightly due to the brittleness.

The seventh row of Table 3 shows the data of 1% ISPR-1 catalyzed paint. The resulting data from EIS showed that the impedance at low frequency was on the order of 10^{10} ohms \cdot cm². The Tg using 1% ISPR-1 was 22 °C. After the paint was exposed to a temperature of 300 °C, the Tg increased to 65 °C. The crosslinking density of the polymer increased. After exposure to a 3% salt solution for 66 days, there was no discoloration of the paint. The salt water immersion study was done in duplicate. Mixed results showed no paint removal along the scribe after removal of the Duck brand tape (conforming to 5A according to ASTM method D3359 test method A) and very few tiny blisters less than 1 mm in diameter removed around the scribe. The tiny blister removal may be due to paint defects. The pencil hardness of the paint was F.

0.5% and 0.75% of ISPR-2 were also studied as the acid additive (last two rows of Table 3). The results from EIS were reproducible. All the panels showed an impedance on the order of 10^9 ohms \cdot cm² at low frequency, which is indicative of a

good protective barrier. The Tg's for the 0.5% and 0.75% ISPR-2 were 18 °C and 34 °C, respectively. After the paint film had been to 300 °C, the Tg increased to 48 °C for 0.5% ISPR-2 and 55 °C for 0.75 ISPR-2. Therefore, the crosslinking density increased after exposure to high temperatures when using both 0.5% and 0.75% ISPR-2. After the panel had been submerged in a salt solution for 66 days, the tape applied to the 0.75% ISPR-2 panels removed blisters around the scribe that were around 3 mm in diameter. The saltwater immersion test for the 0.5% ISPR painted panels salt was not reproducible. One panel had no paint removal and was evaluated as 5A in ASTM method D3359 test method A. The second one had a clump of blisters removed at the bottom of the scribe (~ 2 mm in diameter). The pencil hardness of the paint was HB.

Figure 17 shows painted galvanized steel panels of polyester-melamine paint catalyzed by (a) ISPR, and (b) p-TSA cured at 400 °C for 400 seconds. A paint yellowing is observed in (b), but not in (a). It has been demonstrated that the *in-situ* phosphatizing reagents (ISPRs) can be used to replace para-toluene sulfonic acid (p-TSA) as acid catalyst in polyester-melamine polymerization. First, ISPRs lead to a preferred co-condensation reaction and give a denser and lesser defects paint film. Second, ISPRs inhibit the overbake softening and provide a wider temperature range for thermal curing (particularly, in coil coating application). Third, ISPRs act in both phosphate chemistry and polymer chemistry, thus no residual ISPRs remain in paint films to cause side effect in paint film performance. Fourth, ISPRs prevent the "yellowing" problem observed commonly in polyester-melamine systems.

Throughout this application, various publications, including United States patents, are referenced by author and year and patents by number. Full citations for the publications are listed below. The disclosures of these publications and patents in their entireties are hereby incorporated by reference into this application in order to more fully describe the state of the art to which this invention pertains.

The invention has been described in an illustrative manner, and it is to be understood that the terminology that has been used is intended to be in the nature of words of description rather than of limitation.

5

Obviously, many modifications and variations of the present invention are possible in light of the above teachings. It is, therefore, to be understood that within the scope of the described invention, the invention can be practiced otherwise than as specifically described.

10

References

1. MIL-PRF-85582, DaD Performance Specification, Primer Coating: Epoxy, waterborne.
5
2. MIL-PRF-23377, DaD Performance Specification, Primer Coating: Epoxy, High- Solids.
3. BMS 10-11 V Chemical and Solvent Resistant Finish.
10
4. BMS 10- 79L Urethane Compatible Corrosion Resistant Primer.
5. Lin, C. T., Lin, P., Hsaio, M. W., Meldrum, D. A., and Martin, F. L., "Chemistry of single-step phosphate/paint systems," *Ind. Eng. Chem. Res.*,
15 vol. 3, 1992, pp. 424-430.
- 6; Lin, C. T., Lin. P., and Quitian- Puello, F., "Interfacial chemistry of a single-step phosphate/paint systems," *Ind. Eng. Chem. Res.*, vol. 32, 1993, pp. 818-825.
20
7. Lin, C. T. "Additive package for *in-situ* phosphatizing paint, paint and method," U.S. Patent 5,322,870;1994.
8. Li, L., and Lin, C. T., "SEM-EDS investigations of self-phosphating
25 coatings," *Ind. Eng. Chem Res.*, vol. 33, 1994, pp. 3241-3246.
9. Yu, T., and Lin, C. T., "Chemical Affinity of *In-Situ* Phosphatizing Reagents on Cold-Rolled Steel," *J: Phys. Chem.*, Vol. 99, No. 19, 1995, pp. 7613-7620.
- 30 10. Whitten, M. C., and Lin, C. T., "Coating Performance of Polyester-Melamine Enamels Catalyzed by an *In-Situ* Phosphatizing Reagent on aluminum," *Ind. Eng. Chem. Res.*, vol. 38, 1999, pp. 3903-3910.

11. Yu, T., and Lin, C. T., "*In-situ* phosphatizing coatings III: A water-reducible alkyd baking enamel," *J Coatings. Tech.*, vol. 71, 1999, pp. 87-96.
12. Whitten, M. C., and Lin, C. T., "An *in-situ* phosphatizing coating on 2024 T3 aluminum coupons," *Progress in Organic Coatings*, vol. 38, 2000, pp. 151-162.
13. Lin, C. T., "Green chemistry *in-situ* phosphatizing coatings," *Progress in Organic Coatings*, vol. 42, 2001, pp. 226-235.
14. Paint and coating testing manual. 14th edition of the Gardner-Sward handbook; Koleske, J. V. Eds.; ASTM manual series: MNL 17, ASTM PCN 28-017095-14: Philadelphia, PA, 1995.
15. Skydrol manufactured by Monsanto Company is a mixture of butyl phosphates and additives.
16. MIL-PRF-85285C Type 1, DaD Performance Specification (US Navy), Coating: Polyurethane, High-Solids.
17. Filiform test involves a primer and polyurethane topcoat system. The total system is scribed and subjected to 60 seconds in concentrated HCl vapor and then immediately placing it in a chamber with 80% RH and 104 °F for 1000 hours. After the test, the painted panel shall not exhibit filiform corrosion extended beyond " " from the scribe.
18. Scantlebury, J. D., Ro, K. N., and Eden, D. A., "Electrochemical corrosion testing," Mansfeld, F., and Bertocci, U., Eds., *Anier. Soc. Test. Mater. (ASTM)*: Philadelphia, 1981; STP 727, p. 187.
19. Silverstein, R. M., Bassler, G. C., and Morrill, T. C., "Spectrometric identification of organic compounds," 4th Ed., John Wiley & Sons, Inc.: New York, 1981.

20. Akiyoshi, O., Takahashi, K., and Ikeda, M., "Infrared study of trivalent cations B and Fe in amorphous and crystalline phosphates," *J. Mater. Sci. Lett.*, vol. 3, 1984, p. 36.
- 5 21. Whitten, M. C., Burke, V. J., Neuder, H. A., Lin, C. T., "Simultaneous Acid Catalysis and In-Situ Phosphatization Using a Polyester-Melamine Paint: A Surface Phosphatization Study," *Ind. Eng. Chem. Res.*, vol. 42, 2003, p. 3671-3679.

CLAIMS

What is claimed is:

- 5 1. A coating composition comprising:
a resin;
a phosphatizing reagent; and
at least one compound selected from the group consisting essentially
of a metal chelating agent and a silicating agent, wherein the composition is
10 an *in situ* self-phosphatizing coating composition.
2. The coating according to claim 1, wherein said metal chelating agent is
selected from the group consisting essentially of mono, di, and tri -
organofunctional silanes and diethyldithiocarbamic acid, salts .
- 15 3. The coating according to claim 1, wherein said phosphatizing reagent
is selected from the group consisting essentially of organic phosphoric acids,
organic phosphonic acids, and esters thereof.
- 20 4. The coating according to claim 1, wherein said silicating agent is an
ion-exchanged silica gel.
5. The coating according to claim 1, wherein said resin is selected from
the group consisting essentially of alkyd resins, acrylic resins, polyurethane
25 resins, phenol formaldehyde resins, polyester resins, epoxy resins, and alkyl
vinyl resins.
6. The coating according to claim 1, further including a solvent.
- 30 7. The coating according to claim 6, wherein said solvent is a hazardous
air pollutant -free solvent.
8. The coating according to claim 1, further including a surfactant.

9. The coating according to claim 8, wherein said surfactant is selected from the group consisting essentially of oxyalkylated alkyl phenols, N-lauroylsarcosine, and sodium dioctyl sulfosuccinate.
- 5 10. The coating according to claim 1, further including at least one metal salt.
11. The coating according to claim 1, further including an amine.
- 10 12. A substrate having the coating of claim 1 on a surface thereof.
13. A method of coating an article by applying the coating of claim 1 to a surface of the substrate.
- 15 14. The method according to claim 13, wherein said applying step includes spraying the coating on the substrate.
15. The method according to claim 13, wherein said applying step includes painting the coating on the substrate.
- 20 16. A method of protecting a surface of a substrate by coating the composition of claim 1 to the surface and curing the coating on the surface.
17. The method according to claim 16, wherein said curing step includes drying the coating.
- 25 18. The method according to claim 17, wherein said drying step include drying the coating using a method selected from the group consisting essentially of heating, applying UV light, and air-drying.
19. The method according to claim 17, wherein said curing step includes forming *in situ* a self-phosphatizing coating.
- 30

19. A method of forming an *in situ* self-phosphatizing single-layer coating by combining a phosphatizing reagent and a metal chelating agent with a coating.

- 5 20. The method according to claim 19, wherein said combining step includes adding a silicating agent to the coating.

21. An additive package comprising:
a resin;
10 a phosphatizing reagent; and
at least one compound selected from the group consisting essentially of a metal chelating agent and a silicating agent, wherein the package creates an *in situ* self-phosphatizing coating.

15

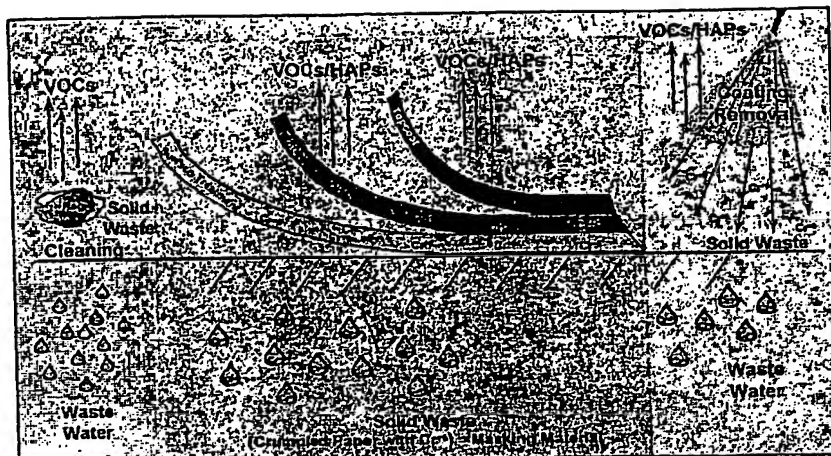


Figure 1.

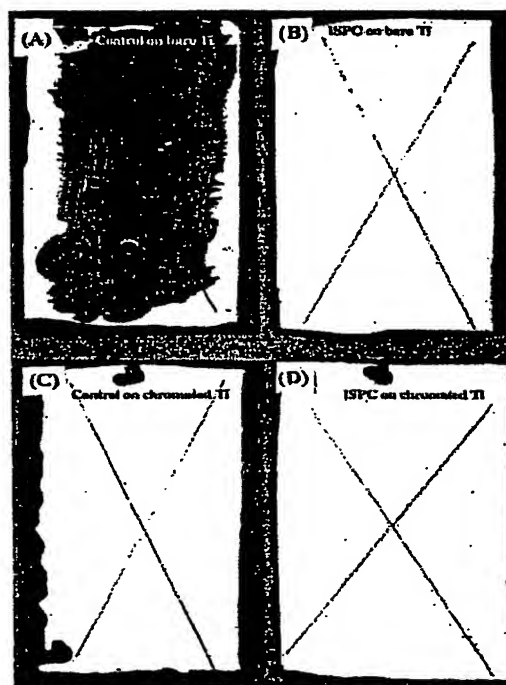


Figure 3.

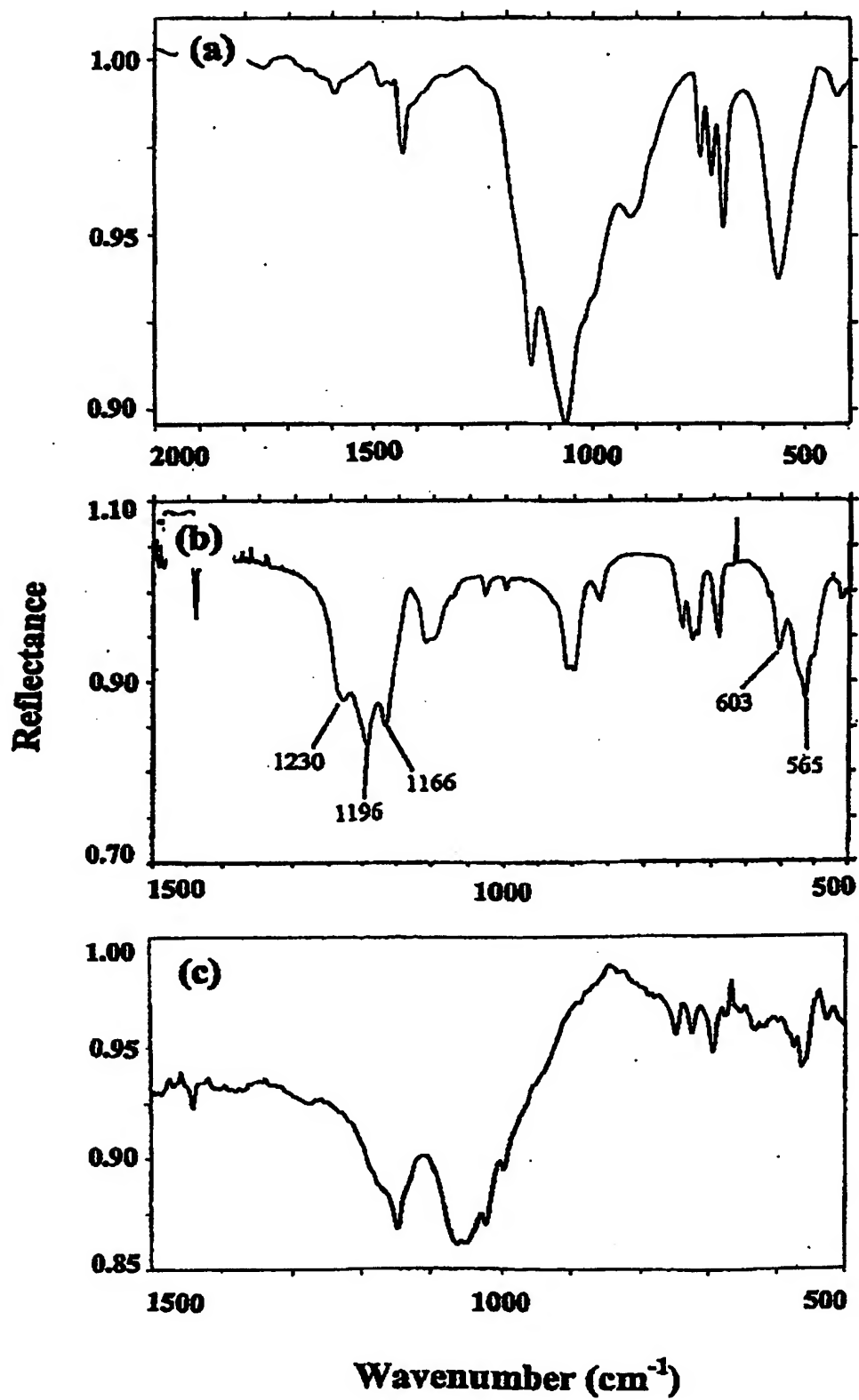


Fig. 2

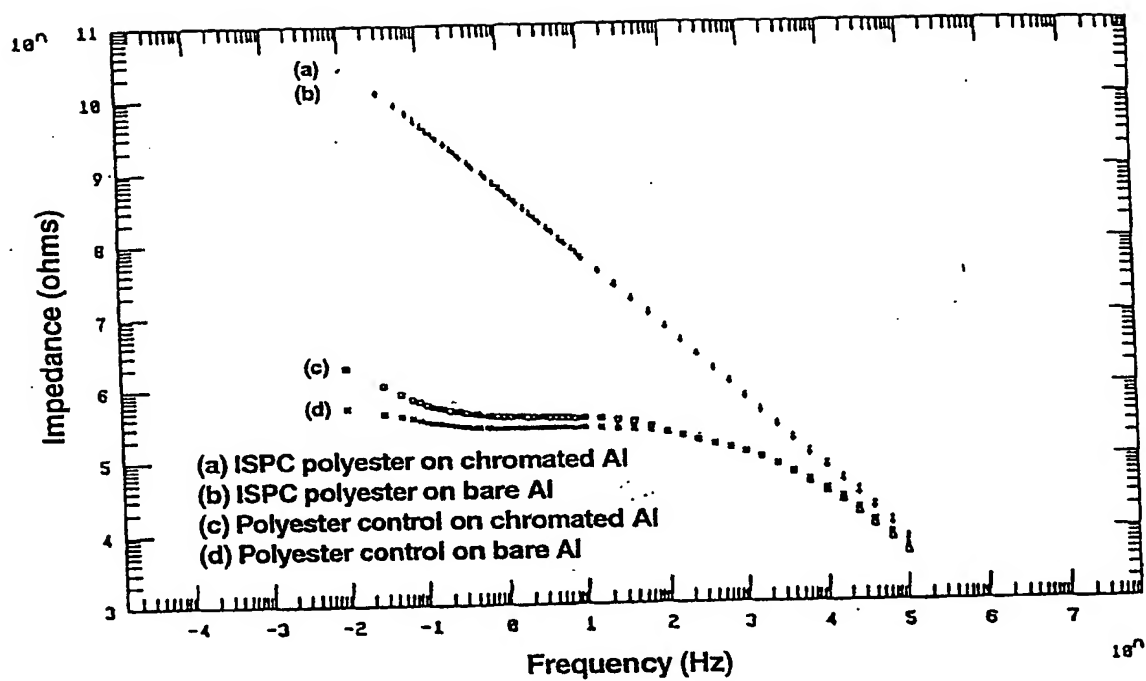


Figure 4.

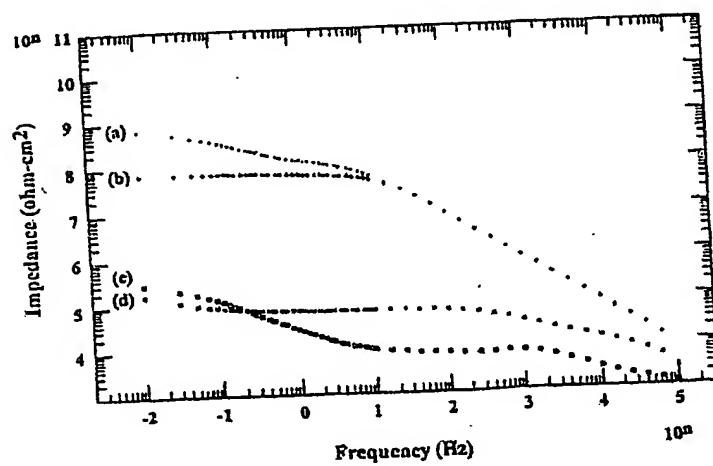


Figure 5.

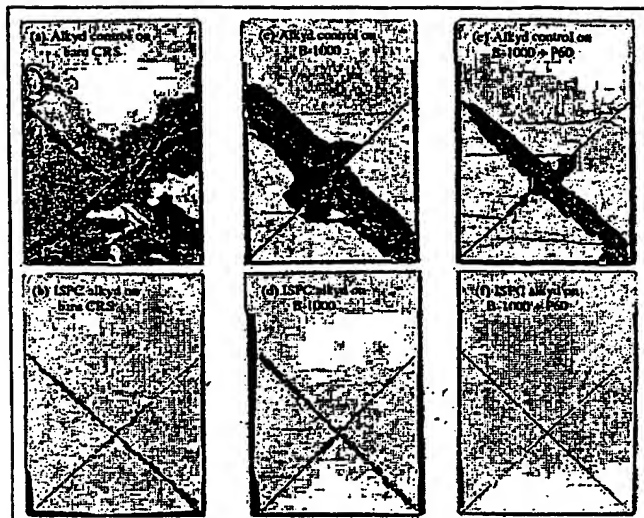


Figure 6.

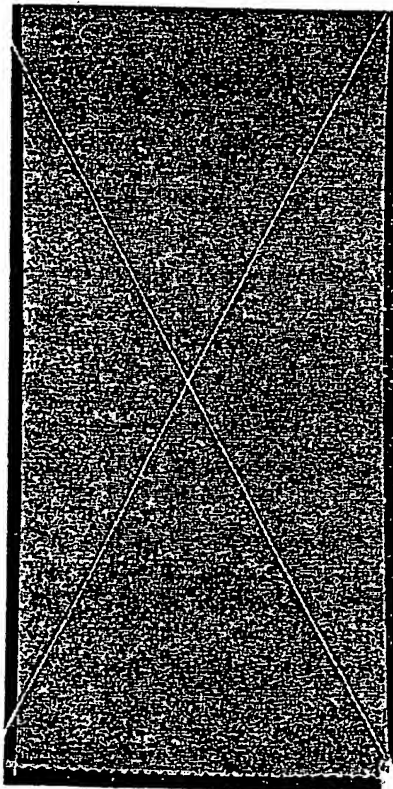
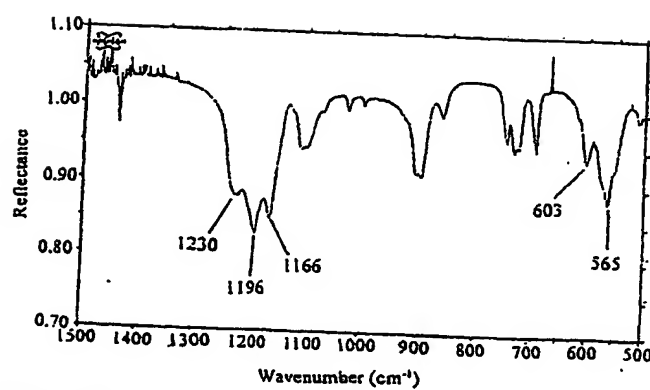
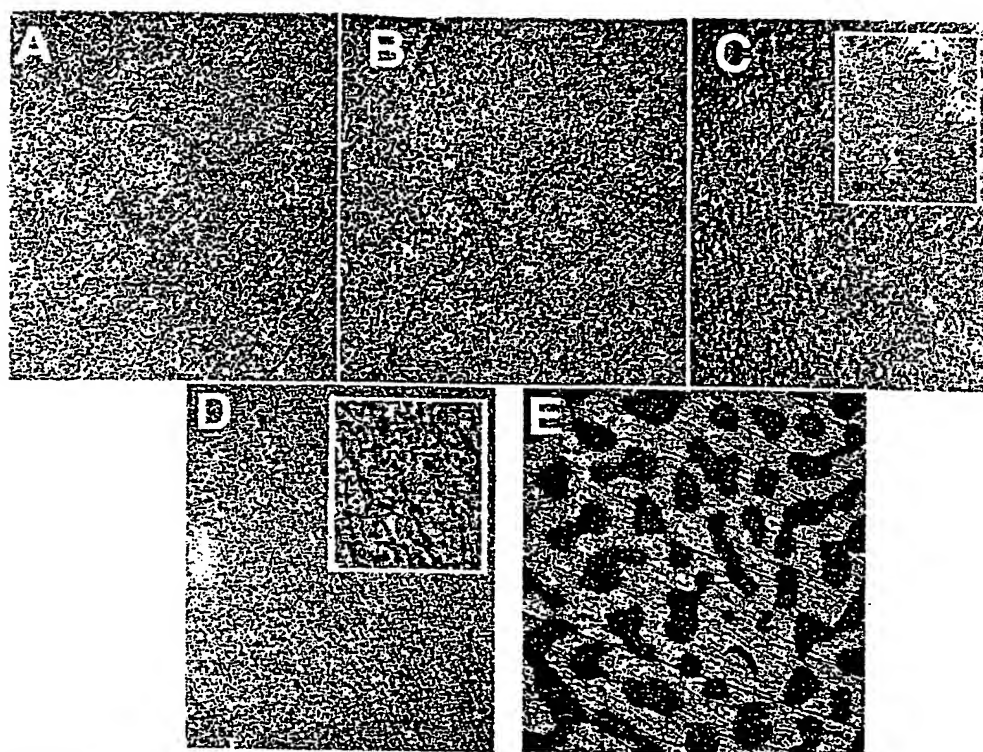


Figure 7

*Figure 8**Figure 9*

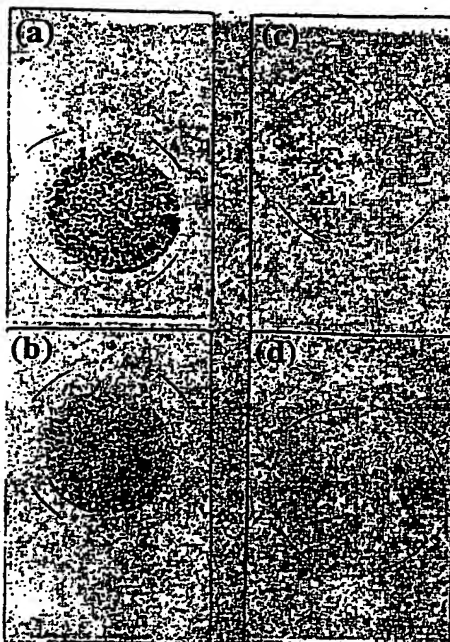


Figure 10

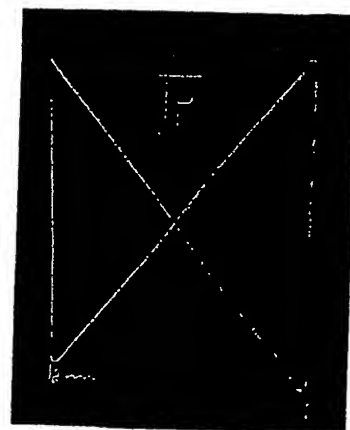
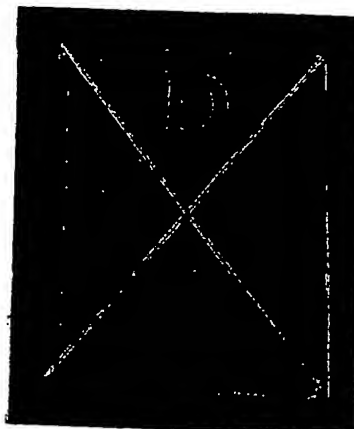
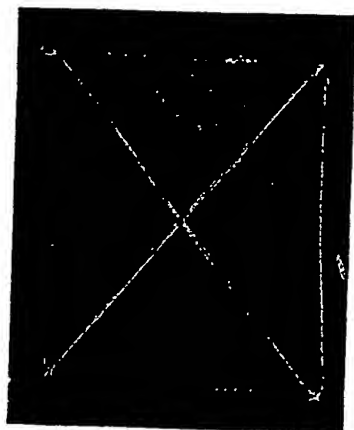
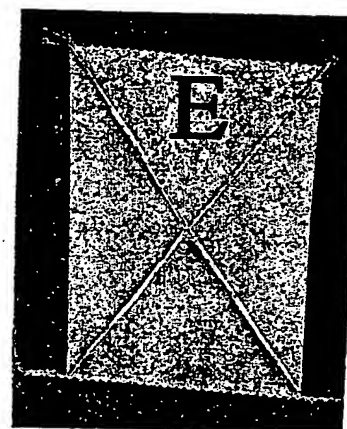
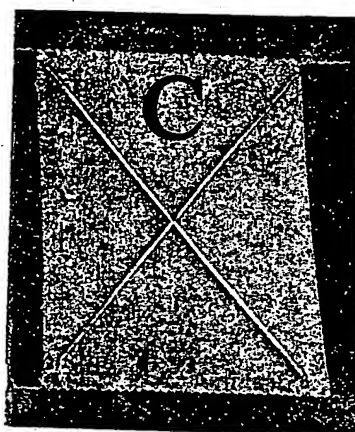
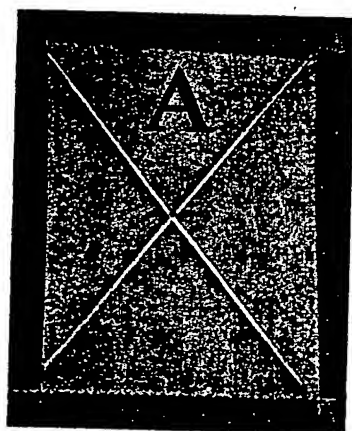


Fig. 11

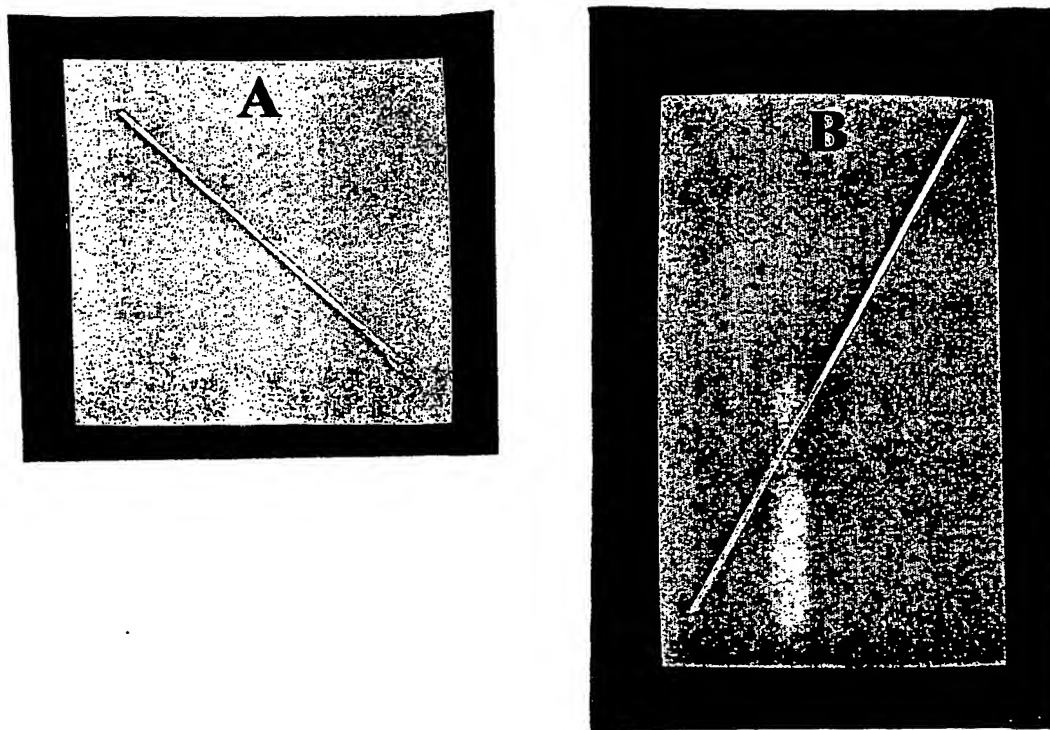


Fig. 12

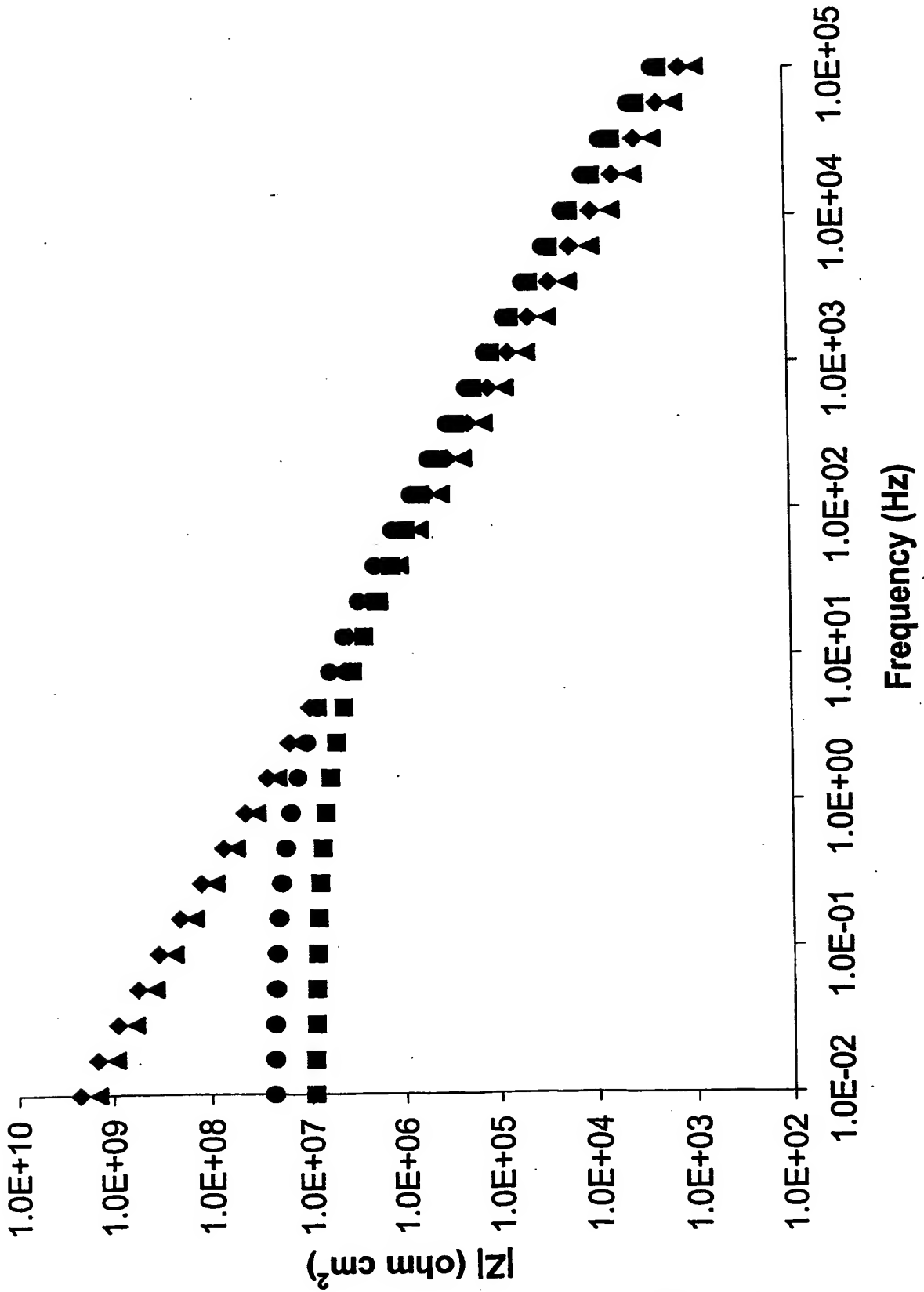


Figure 13

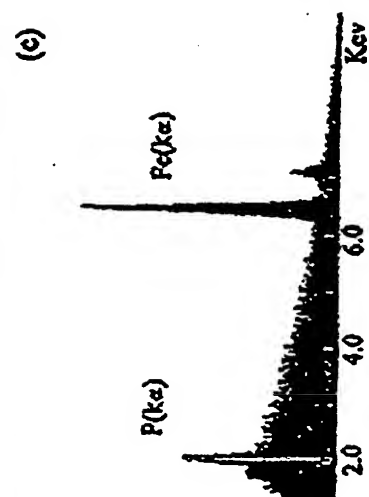
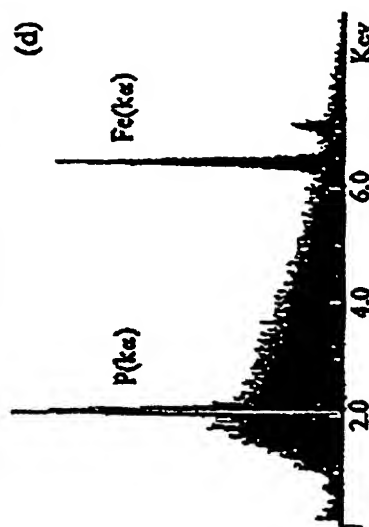
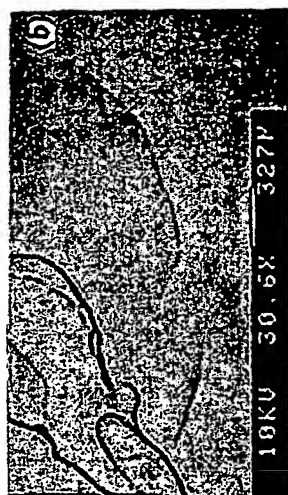


Fig 14

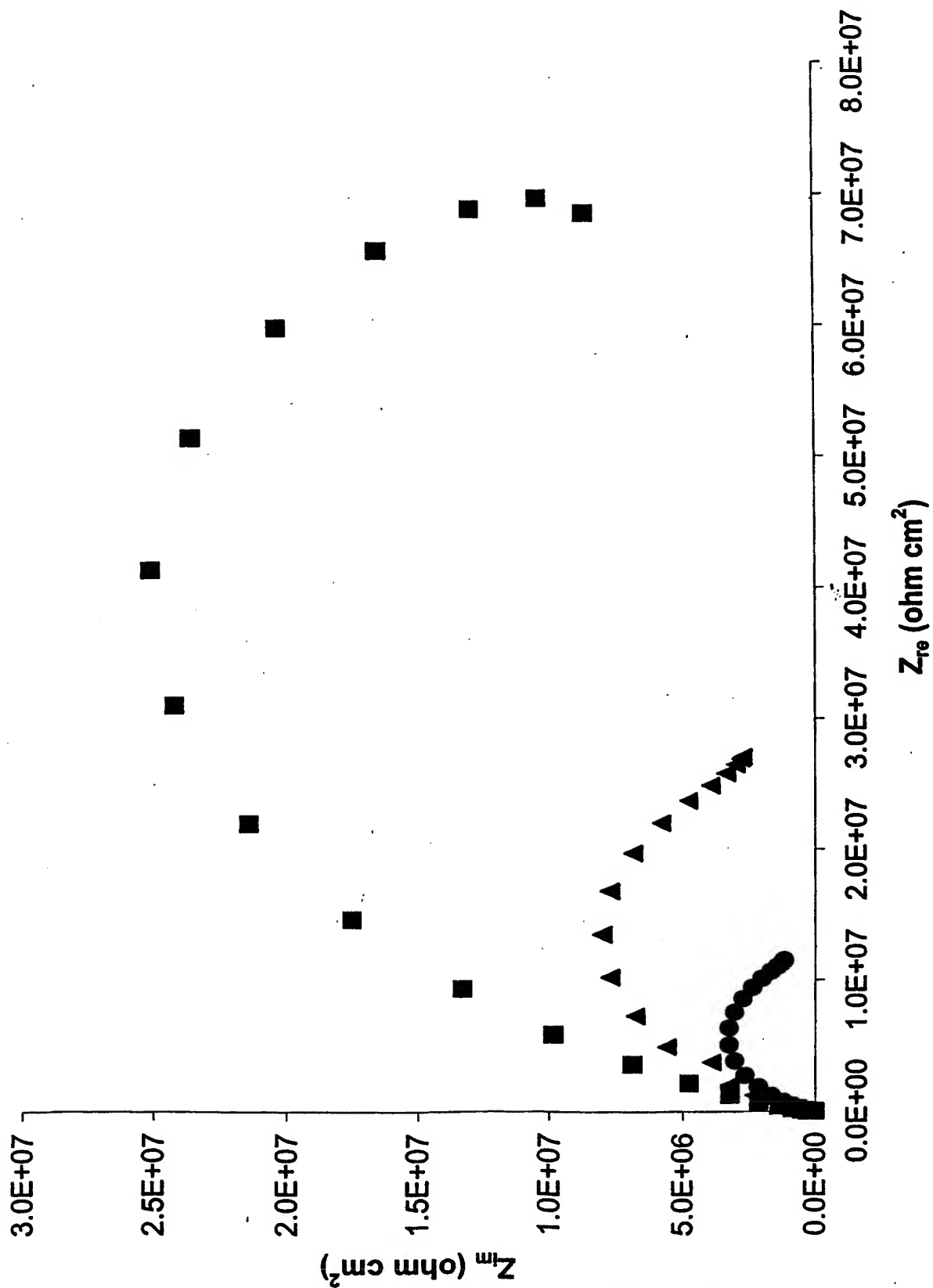
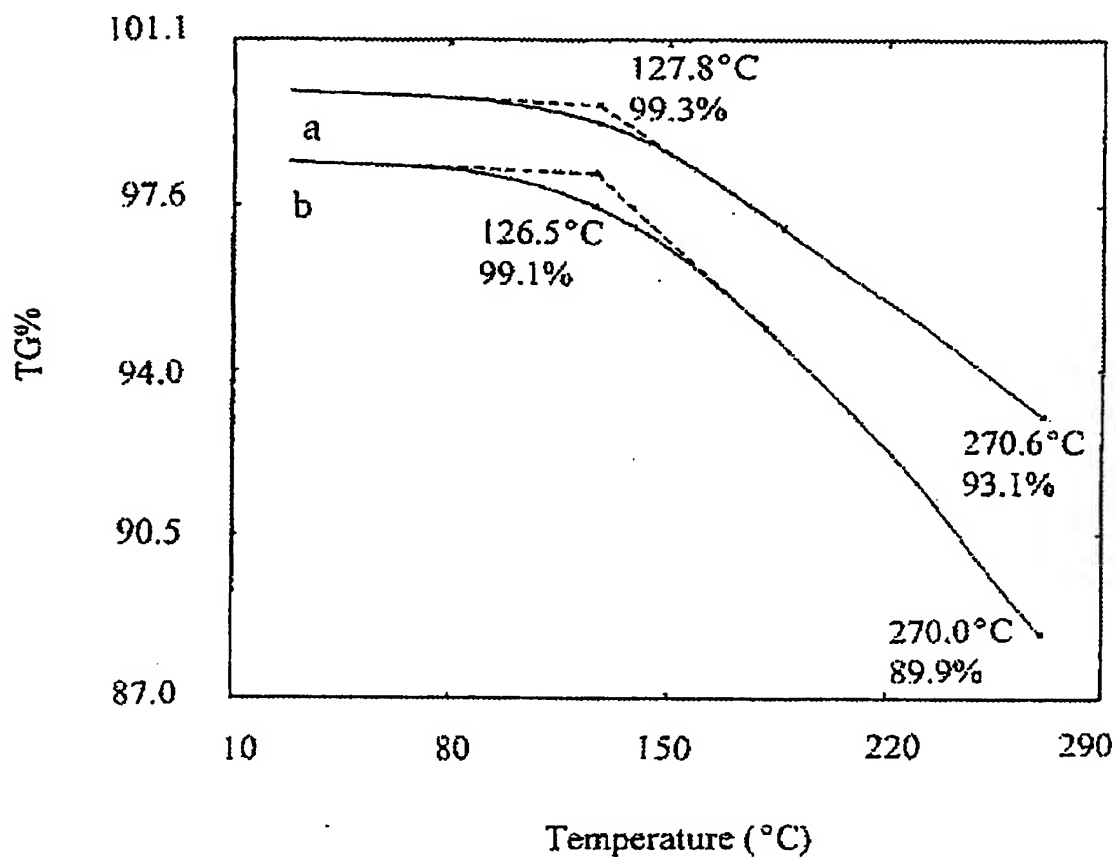


Fig. 15

Figure 16. shows TGA scans of polyester-melamine paint films catalyzed by (a) 3 % ISPR and (b) 3 % Cypat 4040 (p-TSA). The ISPR catalyst paint is thermally stable. More thermal decomposition occurs when using p-TSA as the catalyst.



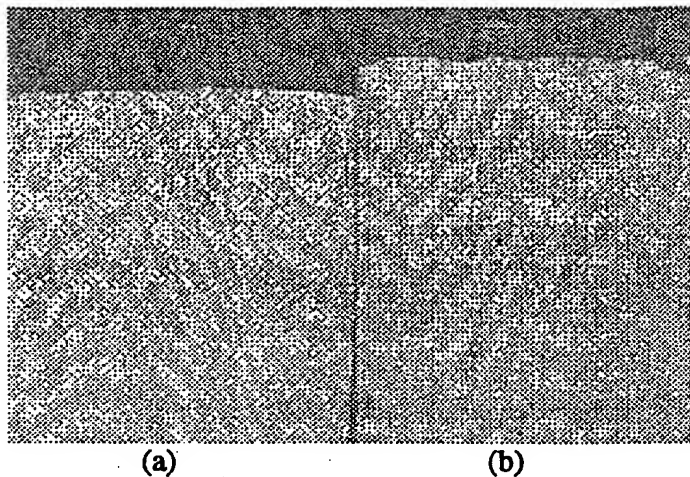


Figure 17. shows painted galvanized steel of polyester-melamine catalyzed by (a) ISPR and (b) p-TSA cured at 400 °C for 40 second. A paint yellowing is observed in (b), but not in (a)

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US03/31419

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) : B05D 3/02; B32B 15/08, 15/18, 27/32, 27/38, 27/40, 27/42; C23C 22/00, 22/68, 30/00
US CL : 106/14.05, 14.12, 14.15, 14.21, 14.41, 14.44; 148/250, 251; 427/386, 387, 388.1, 388.3, 397.7;

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
U.S. : Please See Continuation Sheet

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
Please See Continuation Sheet

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X, P	US 6,475,300 B2 (SHIMAKURA et al) 5 November, 2002 (05.11.2002) col. 2 l. 5-19, col. 2 l. 46-67, col. 3 l. 19-30, col. 4 l. 9-10, col. 4 l. 23-30, col. 4 l. 47-55, col. 5, l. 2-10, col. 6 l. 16-20, col. 6 l. 39-67	1-2, 4-7, 10-21
A	US 6,083,308 A (FLETCHER) 4 July, 2000 (04.07.2000)	
A	US 5,994,447 A (SHIM et al) 30 November, 1999 (30.11.1999)	

☐ Further documents are listed in the continuation of Box C.

☐ See patent family annex.

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Date of the actual completion of the international search

07 February 2004 (07.02.2004)

Date of mailing of the international search report

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INTERNATIONAL SEARCH REPORT

PCT/US03/31419

Continuation of B. FIELDS SEARCHED Item 1:

106/14.05, 14.12, 14.15, 14.21, 14.41, 14.44; 148/250, 251; 427/386, 387, 388.1, 388.3, 397.7; 428/413, 418, 446, 450, 472.1, 480, 500, 524

Continuation of B. FIELDS SEARCHED Item 3:

EAST

search terms, phosphatiz?, binder, acrylic, acryl, polyacrylate, epoxy, polyurethane, phenol formaldehyde, organophos?, anti-corrosion, corrosion resistant, silane, organosilicon, organosilane, silica silicon dioxide, metal chelate, coating, paint, surfactant, emulsifier, surface active

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